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3D printing of stimuli-responsive hydrogel materials: Literature review and emerging applications

Zia Ullah Arif[a,1,*], **Muhammad Yasir Khalid**[b,1,*], **Ali Tariq**[c], **Mokarram Hossain**[d,*], **Rehan Umer**[b]

[a] Department of Mechanical Engineering, University of Southampton, Southampton SO17 1BJ, United Kingdom
[b] Department of Aerospace Engineering, Khalifa University of Science and Technology, PO Box: 127788, Abu Dhabi, United Arab Emirates
[c] Department of Mechanical Engineering, University of Management & Technology Lahore, Sialkot Campus, 51041 Pakistan
[d] Zienkiewicz Institute for Modelling, Data and AI, Faculty of Science and Engineering, Swansea University, SA1 8EN Swansea, UK

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Additive manufacturing (AM) aka three-dimensional (3D) printing has been a well-established and unparalleled technology, which is expanding the boundaries of materials science and is exhibiting an enormous potential to fabricate intricate geometries for healthcare, electronics, and construction sectors. In the contemporary era, the combination of AM technology and stimuli-responsive hydrogels (SRHs) helps to create dynamic and functional structures with extreme accuracy, which are capable of changing their shape, functional, or mechanical properties in response to environmental cues such as humidity, heat, light, pH, magnetic field, electric field, etc. 3D printing of SRHs permits the creation of on-demand dynamically controllable shapes with excellent control over various properties such as self-repair, self-assembly, multi-functionality, etc. These properties accelerate researchers to think of unthinkable applications. Additively manufactured objects have shown excellent potential in applications like tissue engineering, drug delivery, soft robots, sensors, and other biomedical devices. The current review provides recent progress in the 3D printing of SRHs, with more focus on their 3D printing

Abbreviations: 3D, three-dimensional; 4D, four-dimensional; βCD, β-cyclodextrin; AA, acrylic acid; AA-MA, methacrylated alginate; AM, additive manufacturing; CAD, computer-aided design; CMCS, carboxymethyl chitosan; CNC, cellulose nanocrystals; CNF, cellulose nanofiber; CNT, carbon nanotube; DOX, doxorubicin; DLP, digital light processing; DIW, direct ink writing; EC, ethyl cellulose; FDM, fused deposition modeling; GelMA, gelatin methacryloyl; HAMA, methacrylated hyaluronic acid; IJP, Inkjet printing; LCE, liquid crystal elastomer; MNPs, magnetic nanoparticles; MWCNTs, multi-walled carbon nanotubes; NIR, near-infrared; PAA, poly(acrylic acid); PAAM, polyacrylamide; PANI, polyaniline; PBF, powder bed fusion; PCL, polycaprolactone; PCLDMA, polycaprolactone dimethacrylate; PDA, polydopamine; PDMS, poly(dimethylsiloxane); PEGDA, polyethylene glycol diacrylate; PEGDMA, poly(ethylene glycol) dimethacrylate; PLA, polylactic acid; PNIPAM, poly(N-isopropylacrylamide); PPy, polypyrrole; PU, Polyurethane; PVA, poly(vinyl alcohol); rGO, reduced graphene oxide; SA, sodium alginate; SAMA, sodium alginate methacrylate; SMA, shape memory alloy; SME, shape memory effect; SMH, shape memory hydrogel; SMP, Shape memory polymer; SLA, stereolithography; SPIONs, superparamagnetic iron oxide nanoparticles; SRH, stimuli-responsive hydrogel; SRP, stimuli-responsive polymer; μSLA, Micro-stereolithography; TCP, tricalcium phosphate; TPP, two-photon polymerization; TPU, thermoplastic polyurethane; UV, ultraviolet.

* Corresponding authors.
E-mail addresses: zia.arif@soton.ac.uk (Z.U. Arif), yasirkhalid94@gmail.com, 100062624@ku.ac.ae (M.Y. Khalid), mokarram.hossain@swansea.ac.uk (M. Hossain).

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[1] These authors contributed equally to this work and are co-first authors.

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techniques, stimuli mechanisms, shape-morphing behaviors, and their functional applications. Finally, current trends and future roadmap of additively manufactured smart structures for different applications have also been presented, which will be helpful for future research. This review holds great promise for providing fundamental knowledge about SRHs to fabricate structures for diverse applications.

1 Introduction

The Additive manufacturing (AM) also known as the three-dimensional (3D) printing, rapid prototyping, or solid freeform fabrication, fabricates complex, multi-functional, and multi-material components directly from computer-aided design (CAD) files, by depositing materials in layer-by-layer fashion [1–4]. This novel concept was initially coined by Charles W. Hull in 1984. Over the years, 3D printing has been rapidly developed and has witnessed a significant advancement in methods, materials, technologies, and applications [5–7]. According to ASTM/F2921, the 3D printing technology is further classified into material extrusion, powder bed fusion, material jetting, binder jetting, direct energy deposition, vat photopolymerization, and sheet lamination techniques [8–10]. 3D printing techniques can generate fully-customized objects with good precision, high energy efficiency, design flexibility, and reduced waste compared to the traditional manufacturing processes [11–14]. Furthermore, compared to conventional manufacturing technologies, 3D printing technology does not require molds, machining or tooling. It can be used for metals, alloys, polymers, ceramics, and multi-materials to develop fully-customized and precise structures [15–19]. As such, 3D printing is extensively used in a wide range of industries like automotive, aerospace, energy, food, robotics, electronics, chemical, biomedical, etc. [20–23]. However, 3D printing usually develops unresponsive and static structures [24–26].

To overcome this issue, in 2013, Tibbits demonstrated the concept of four-dimensional (4D) printing [27–31]. This concept uses the combination of 3D printing and stimuli-responsive materials to induce shape morphing effect with time as the 4th dimension, after fabrication upon environmental stimulations, thus, uncovering new advancements in the AM field [32–36]. However, with the passage of time, it was found that some structures change their properties such as color or stiffness instead of shape under external stimuli [37–39]. The most recent definition of 4D printing takes this possibility into account together with the programmability and predictability of the response [40–43].

4D printing depends on 3D printing technique, stimulus type, stimuli-responsive material, interaction mechanism, as well as mathematical modeling [[38,44,45]. These stimuli-responsive materials exhibit self-assembly, self-sensing, self-actuating, and shape memory features, which are highly suitable for developing dynamic and complex structures [46–49]. Stimuli-responsive materials are classified into stimuli-responsive soft polymers (SRPs), liquid crystal elastomers (LCEs), and stimuli-responsive hydrogels (SRHs), which have shown sensitiveness to external stimuli such as light, heat, electric field, magnetic field, humidity, etc. [50–55]. Additionally, these materials exhibit the potential to fabricate interactive and adaptive structures for biomedical, aerospace, electronics, and other intelligent applications [56–61]. Shape-memory feature of SRH materials can help to fabricate time-dependent 3D structures, which switch between different configurations upon external stimulations [62–64]. Furthermore, nature-inspired systems with shape morphing abilities instigate the scientists to develop bioinspired designs and patterns using the combination of stimuli-responsive materials and 3D printing processes [65–68]. Shape-memory materials are further classified into shape-memory polymers (SMPs), shape-memory alloys (SMAs) and shape-memory hydrogels (SMHs) [69–73]. Fig. 1 depicts the key characteristics of SMPs, SMAs and SMHs. It is evident from Fig. 1, that SMH provides a good balance of various properties such as biodegradability, self-healing etc. biocompatibility in comparison to its competitive materials.

Stimuli-responsive hydrogels are the class of stimuli-responsive materials, which have found their applications in 4D printing, thanks to their sensitiveness to specific external stimuli and extraordinary soft material properties [74–78]. These hydrogels are responsive to electric field, pH, heat, and magnetic field, and are used to fabricate diverse structures with excellent controllability and adaptability [79–81]. Fig. 2 shows the publication trends of 3D printing of SRHs across the different years.

1.1 Scope of the review

In recent years, there have been various attempts made by researchers to summarize the 3D printing of SRHs to grasp knowledge of 3D printing techniques and various potential stimuli. For instance, Champeau et al. [82] provided the state-of-the-art 4D printing of smart hydrogels, considering the material's perspective. This article presents an exhaustive, authoritative, and critical review of the 3D printing of SRHs for developing multi-functional structures for ground-breaking applications. Additionally, the review aims to provide the recent advancements in the 3D printing of SRHs.

1.2 Stimuli-responsive hydrogels

Hydrogels contain large amounts of water entrapped by 3D cross-linked molecular networks. Through covalent bonding or noncovalent interactions, the intriguing network of a hydrogel is established through which it contains a large amount of water for a long time in a liquid environment [83–85]. As much as 99% of the weight of a hydrogel can be water, thus, making them promising materials for water-enriched biological environments such as the human body. Fig. 3 depicts the unique characteristics of hydrogels that make them suitable for different engineering fields. The translation of hydrogels into the clinic is mainly due to its various characteristics such as proliferation, cell adhesion, migration, and delivery of small or macro-biomolecules [86–88]. These characteristics are due to the circulation and exchange of nutrients and wastes in hydrogel molecules. Furthermore, their roles in AM are thanks to their diverse capabilities such as additives, suitable degradation

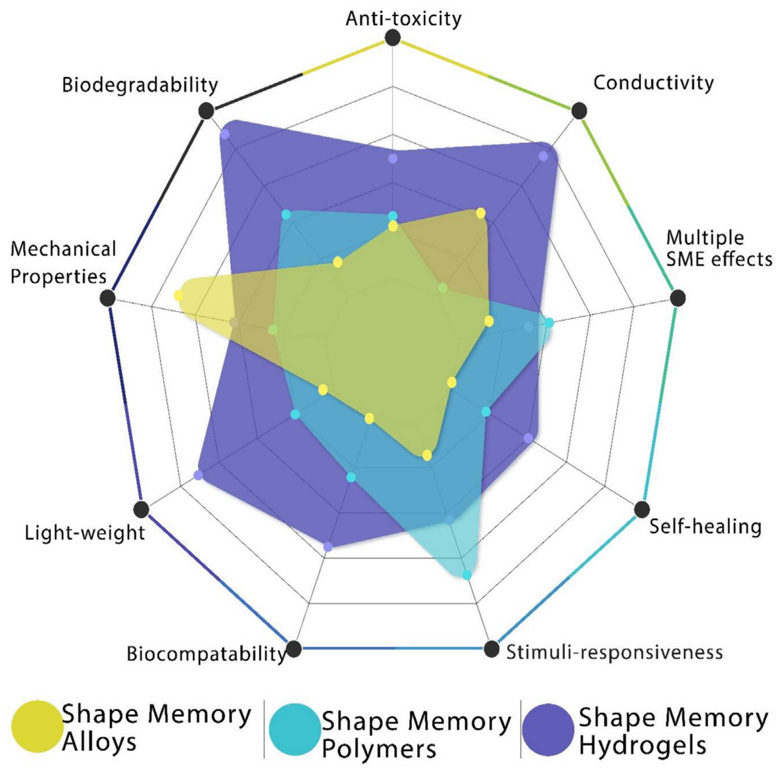


Fig. 1

Comparison between the properties of shape memory materials.

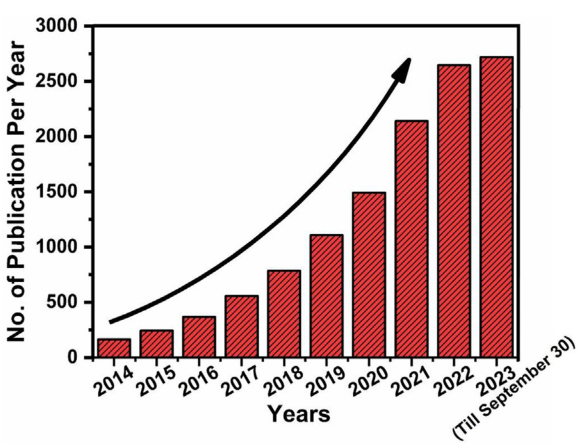


Fig. 2

Publication trends for 3D-printed hydrogels across the different years. (Figure drawn based on the information from Scopus database using "3D printing", and "hydrogel" as keywords).

rate, potential ink materials and stimuli responsiveness [89–92]. Hydrogels reversible movement in response to environmental stimuli have been exploited as actuators and cell culturing for drug delivery and tissue engineering applications [93–96].

With the increasing demand for hydrogels in different engineering applications, research scientists have fabricated SRHs which are also known as "smart hydrogels" or "intelligent hydrogels" [98–100]. SRHs can undergo structural transitions and stimuli-induced volume, thus, showing their suitability for multi-dimensional applications [101]. Table 1 summarizes different stimuli for SRHs, and their advantages and disadvantages. Responsive hydrogels can be synthesized through chemical or physical cross-linking methods [102]. Chemically fabricated hydrogels rely on a covalent bonding of their polymer network and this approach is further classified into grafting-, free radical-, and radiation-polymerization techniques [103]. Whereas, physical cross-linking mainly utilizes hydrogen bonding, hydrophobic, and electrostatic attractions for holding the polymer chains [104]. Hydrogels synthesized by such methods show reversible swelling-deswelling transitions in response to different stimuli. More than one polymer can be used to synthesize SRHs, which makes them highly diverse and can be fitted in multi-functional applications [105–107]. To date, various natural protein-based hydrogels (fibrin, gelatin, silk fibroin, and elastin) [108–111], polysaccharide-based hydrogels (hyaluronic acid, chitosan, and alginate) [112–118], and synthetic hydrogels are effectively used in different 3D/4D printing applications [119–125].

2 3D printing

3D printing or rapid prototyping technology refers to the development of 3D objects with precise dimensions through the layer by layer deposition [155–157]. A wide range of materials from metals and alloys to elastic polymers can be printed by using this technology [158–160]. It can print customized and intricate designs such as complex lattice structures, which cannot be manufactured using conventional manufacturing processes [161–164], as illustrated in Fig. 4. 3D printing technology contains a variety of techniques

Table 1

Advantages and disadvantages of different stimuli, which are used to develop SRH-based structures.

Stimulus	Hydrogel type	Advantages	Disadvantages	Commonly used hydrogels	Ref.
Light	Photo-responsive	i. Remotely controlled ii. The triggering mechanism can be easily controlled iii. Tunable mechanical properties	i. Difficulty in controlling the intensity of light in depth	PNIPAM, PEGDA	[126–129]
Temperature	Thermo-responsive	i. Ease in manufacturing ii. Incorporation of active substance is easier	i. Slow response ii. Compatibility problems	PNIPAM, GelMA, chitosan, chitin, agarose, alginate, methylcellulose	[130–135]
Electric field	Polyelectrolyte	i. Fast actuation ii. Precise response	i. Require electrodes and electrolytes	PANI	[136–140]
Magnetic field	Embedded magnetic particles	i. Remotely controlled	i. Require magnetic particles	Hydrogels containing magnetic particles or magnetic matrices	[141–144]
Humidity	Water-responsive	i. Ease of operation	i. Slow response	CNC, CNF	[145–148]
pH	Acidic or basic	i. Easy to prepare the solution	i. Require pH solution ii. Slow response	PAA, HA, chitosan, alginate	[149–151]
Ions	Ionic	i. Easy to prepare the solution	i. Require ionic solution	PUA, AA, alginate, methylcellulose	[152–154]

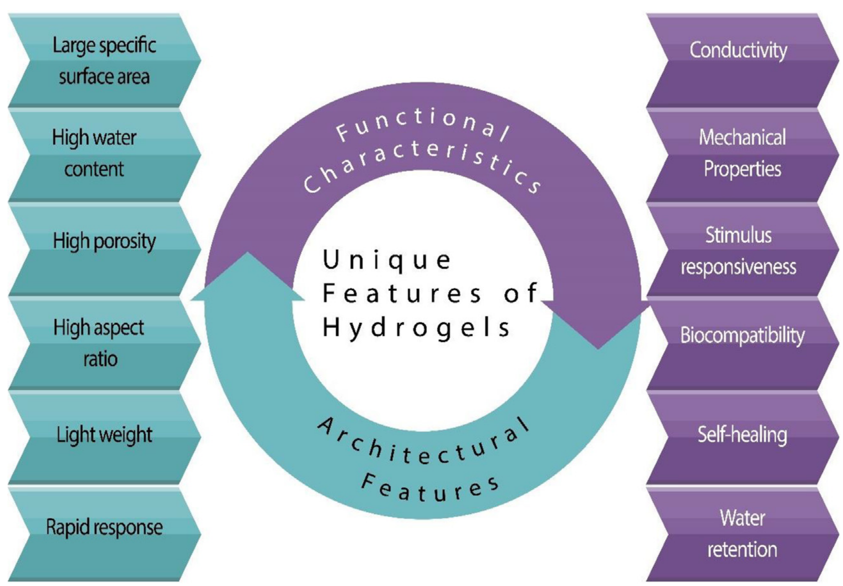


Fig. 3

Distinct features of hydrogels (Figure drawn based on the information provided by ref. [97]).

including extrusion-based printing, vat photopolymerization (stereolithography (SLA), digital light processing (DLP) [165–167], two-photon polymerization (TPP)), material jetting, inkjet printing (IJP), and powder bed fusion (PBF) [168–171]. Rapid prototyping of hydrogels to develop highly customized complex shapes is quite challenging through traditional fabrication techniques including casting and electrospinning. While novel AM opens the great possibility to fabricate 3D permanent shapes, which have shown tremendous potential in developing smart structures [172–175]. 3D printing can be used to fabricate 3D multi-functional products using stimuli-responsive materials especially SRHs [176–180]. SRH-based 3D-printed structures have found their applications in tissue engineering, drug delivery, smart actuating, and micro-gripping applications [181–185]. Nevertheless, not all 3D printing processes apply to printing SRHs, because hydrogels can only be processed under mild conditions [186]. Therefore, this review elucidates 3D printing techniques that are used to process hydrogels only. Table 2 provides an overview of different 3D printing techniques including advantages and disadvantages, which are used to print SRHs.

Extrusion-based printing deposits molten or semi-molten polymers, dispersions, or pastes on a built tray to develop 3D structures layer-by-layer [214–218], as illustrated in Fig. 5(A). It is further classified into fused deposition modeling (FDM) and direct ink writing (DIW) [219–222]. FDM melts solid polymers and extrudes them from a nozzle to fabricate 3D objects

Table 2

Different 3D printing techniques used to print SRHs.

3D printing	Representative hydrogels	Ink viscosity (mPa s)	Resolution (μm)	Advantages	Disadvantages	Applications	Ref.
Extrusion	PNIPAM/k-carrageenan, gelatin, GelMA, alginate, CMCS	$6–30 \times 10^7$	50–1000	i. Widely source of printing inks ii. Low-cost iii. Easy operation iv. Suitable for multi-material fabrication	i. Nozzle clogging ii. Moderate speed	Scaffolds, soft robots, origami structures, edible foods, hyperthermia cancer therapy	[188–195]
SLA	PEGDA, PEGDMA	No limitation	30–500	i. High resolution ii. No clogging issue	i. Material limitation ii. Ink wastage iii. Incomplete/over iv. curing v. High cost	Drug delivery, micro-actuators, micro-fluidic devices	[196–199]
DLP	PEGDA, SA, PAAM	–	15–100	i. High resolution ii. Precise heterogeneous structure iii. No clogging issue iv. High printing speed	i. Material limitation ii. Ink wastage	Smart robots, load-bearing elements, scaffolds	[200–206]
TPP	PNIPAM, PEGDA, GelMA	–	< 1	i. High spatial resolution ii. High control and accuracy iii. Versatile printing technique	i. Only applicable to photo-polymer hydrogel inks with a single material system ii. Slow process	Mobile micro-machines, bio-sensors, milli-grippers, micro-robots	[207–209]
IJP	Alginate, PVA, PANI	2–10	10–500	i. High resolution ii. Suitable for multi-material fabrication iii. High speed iv. Multi-size fabrication	i. Nozzle clogging ii. Moderate precision iii. Poor vertical quality	Micro-scaffolds, electronic devices, smart actuators	[210–213]

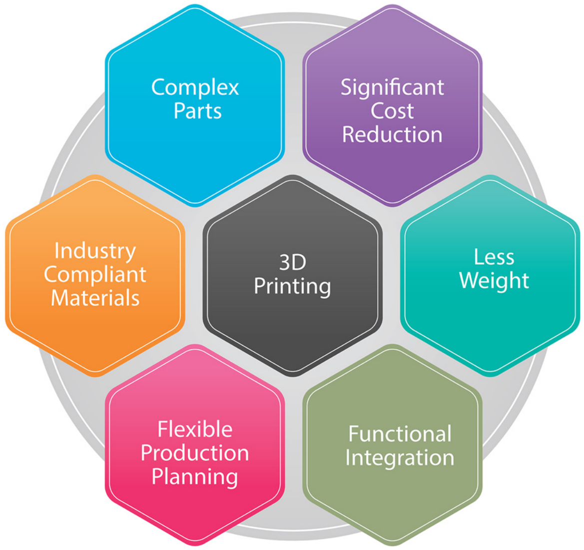


Fig. 4

Technological benefits of 3D printing over conventional manufacturing processes (Figure drawn with the help of ref. [187]).

[223–225]. Although filaments for the FDM are diverse, the utilization of these filaments in 4D printing is limited due to the lack of functional properties [226–228]. Thus, the lack of intelligent filaments has made the FDM process highly complex for 4D printing [229–232]. DIW, a relatively simple 3D printing technique, is conducted through ink extrusion and hardening [233–235]. Therein the dispensed ink in the form of fluid can be extruded via a nozzle and must be quickly hardened to retain the structure after deposition [236–240]. Hydrogel-based structures are mostly fabricated through DIW [241–243]. Furthermore, the fabrication temperature for the DIW printing is quite low compared to the FDM, which prevents the degradation of hydrogel inks [244–246]. This technique is highly suitable for multi-material printing [247–250].

Vat-photopolymerization is another printing approach, which uses liquid resins for polymerization by developing either a linear or a crosslinked network [251–254]. This light-activated approach selectively converts photocurable resins to solid polymers using ultraviolet (UV) of different wave lengths [255–257]. Vat-based technology possesses high adaptability to fabricate 3D objects with high resolution, high speed, and high accuracy [258–260]. The technique is further divided into SLA, DLP, and TPP [261–264]. Fig. 5(B) illustrates the different between SLA and DLP printing. TPP is suitable for developing micro-structures with ultra-high resolution [265–267].

2.1 4D printing

Nature is continuously inspiring the material scientist's community [268]. Nowadays, we see the complex behavior of materials such as changing their shapes in the stimulant environment originating from millions of years of evolution [269,270]. The realization of hydrogel-based precise microstructural devices with complex 2D and 3D structures is possible due to the core efforts of SRHs [271–273]. Researchers are combining smart materials and external stimuli with traditional additive processes [274–276]. This creative concept is directly encoded into diverse structures. Such 4D behavior includes self-assembly (in the absence of traditional driving equipment), self-sensitive, or self-healing [277–280]. 4D printing technology has shown great interest in developing modern living structures with parallel aligned with some sustainable goals such as low environmental impacts with low energy consumption [275] [281,282]. 4D printing uses the same 3D printing techniques to develop dynamic structures using SRH materials. The 3D-printed SRHs in various forms are crucial materials for scaffold development especially for tissue repair [283–285]. This section elucidates the 3D printing of different types of SRHs.

2.2 3D printing of magneto-responsive hydrogels

In recent years, 3D-printed magnetic-driven actuators with complex geometry, and programmable structure have been widely explored [286]. Particularly, patterning magnetic hydrogels through 3D printing offers a wide range of opportunities in navigation and remotely controlled hydrogel actuators. For instance, Simińska-Stann et al. [242] fabricated magnetic hydrogels through multi-material direct printing using polyacrylic acid (PAA) with improved dispersion through magnetic nanoparticles (MNPs). Ca^{2+}-based interactions improved the crosslinking of PAA-MNPs hydrogel. Various patterns of magnetic actuators were printed (Fig. 6(A)) for steerable motion in the

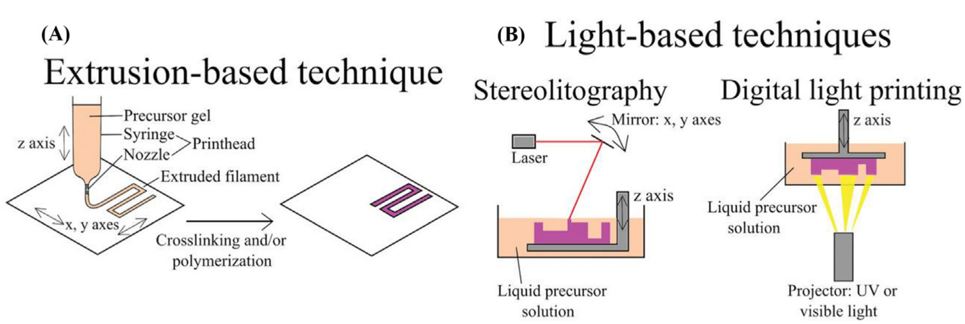


Fig. 5

Light and extrusion-based commonly employed printing techniques used for 3D printing of smart hydrogels (adapted from ref. [82], copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

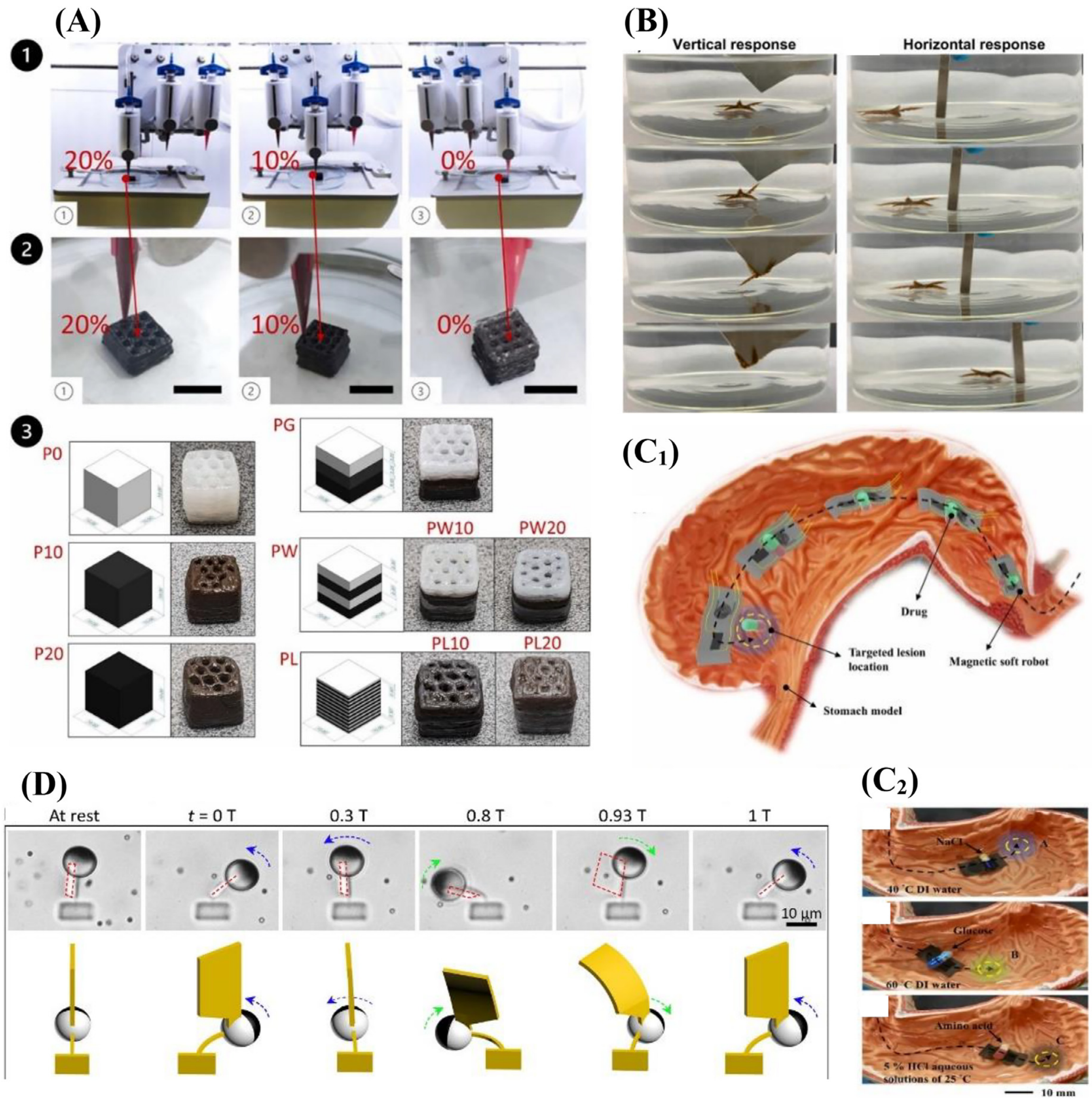


Fig. 6

(A) (1–2) Multi-material printed models of magnetically graded hydrogel cubes with three various inks of PAA/MNPs (3) Single- and multi-material hydrogel structures with various structures designs models on the left side and printed model on the right side (adapted with permission from ref. [242] under the terms of the Creative Commons Attribution license 4.0.); (B) Images of 3D-printed magnetic starfish hydrogels with 1 wt.% SPIONs; The arms swing and attach to it towards the magnet and illustration of hydrogel starfish following the movement of the magnet (adapted with permission from ref. [287] under the terms of the Creative Commons Attribution license 4.0.); (C_1) Magnetic soft robot used for targeted drug delivery in stomach model; (C_2) Experimental illustration of the robot delivering diverse drugs at various temperatures in DI water, next in NaCl capsule to the location 'A' in 40 °C and finally glucose capsule to the location 'B' in 60 °C. The amino acid capsule to the location 'C' in 25 °C 5% HCl aqueous solutions (adapted with permission from ref. [288] copyright 2022 Elsevier B.V.); (D) Microscopic and schematics images demonstrating the deflection of the flag-shaped structures by arrows such as blue for magnetic and green for elastic behaviors (adapted with permission from ref. [290] under a Creative Commons Attribution License 4.0 (CC BY)).

air demonstrating their spatially anisotropic response under a magnetic field. Likewise, Mohammad et al. [287] 3D-printed starfish hydrogels using 2 wt.% superparamagnetic iron oxide nanoparticles (SPIONs) with acrylamide and PEGDA with shape deformation of 10% when swollen. Results showed that the starfish grabbed onto a magnet with all arms under a magnetic field stimulus, as depicted in Fig. 6(B). Furthermore, the printed hydrogels returned to their original formation when the magnetic stimulus was removed and retained their excellent shapes. Thus, these hydrogels have shown potential in magnetically stimulated actuators and soft robotics applications.

Wang et al. [288] printed a millimeter-scale magnetic soft robot using (MWCNTs/PDMS) composites. Furthermore, a dual-sensor configuration-based magnetic soft robot was fabricated from (rGO/PDMS) composites which was printed directly on the surface of neodymium-iron-boron (NdFeB)/PDMS composite substrate. Various functions of the soft robot such as temperature, tactile and electrochemical stimuli were detected and controlled through

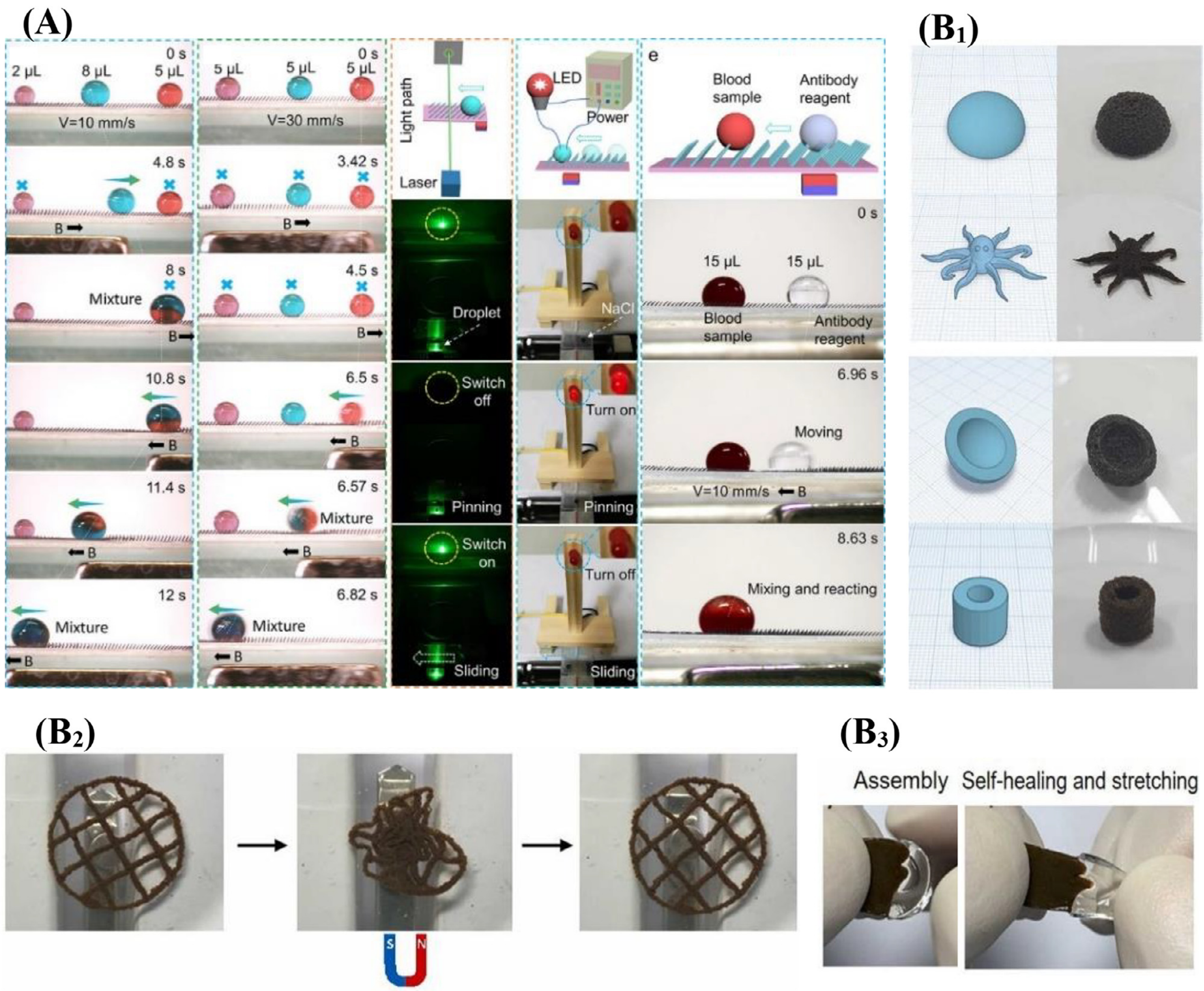


Fig. 7

(A) Ternary droplets selective manipulation under magnetic field function (adapted from ref. [296] copyright 2023 American Chemical Society); (B_1) 3D-printed complex 3D structures (octopus, and tubular) with ferrogel, (B_2) Response of 3D-printed structures under magnetic field stimulus, (B_3) Illustration of self-healing behavior between hydrogel and ferrogel (adapted with permission from ref. [294] copyright 2022 Elsevier B.V.).

electrical responses of the integrated sensors. Drug delivery was carried out during a proof-of-concept demonstration of the soft robot as depicted in Fig. 6(C_1)-Fig. 6(C_2). Moreover, the drug dissolutions made a quantitative evaluation for drug delivery induced by the targeted and the integrated sensors successfully detect the surrounding concentration variations.

Various nanoparticles respond well to magnetic forces or torques generated under magnetic fields, for remote and accurately controlling the actuation behaviors [289]. For instance, Zhang et al. [290] proposed FePt Janus microparticles and silk fibroin (SF) hydrogel-based wirelessly actuated programmable microfluidic cilia for various purposes in healthcare devices. Initial results confirmed that a programmable metachrony with controllable phase differences was observed by adjusting the orientation of the identically magnetized hard FePt Janus microparticles. This allows wave propagation along the cilia array under a rotating magnetic field (globally), as depicted in Fig. 6(D).

Researchers are also continuously employing synergistic combinations of hydrogels with 3D printing for fabricating sophisticated structures effective for numerous biomedical applications [291–293]. Recently, Mun et al. [294] printed magnetic responsive ferrogels/MNPs-based hydrogels using hyaluronic acid (HA) base material with remotely controllable properties Fig. 7(B_1)-Fig. 7(B_2). HA was further as hydrazide-modified (hHA), oxidized (oHA) and improved further by adding adipic acid dihydrazide (ADH) for their self-healing behavior. Results demonstrated that oHA/hHA/ADH-based self-healing properties as presented in Fig. 7(B_3) were observed by adding SPIONs. Also, the remarkable stretchability and structural integrity (= 94.3 ± 1.5%) were noted particularly for tissue engineering applications. The magneto- and electroactive-based structures are highly efficient for many engineering and biomedical applications because they are highly tunable to regulate their performance/functionalities under external

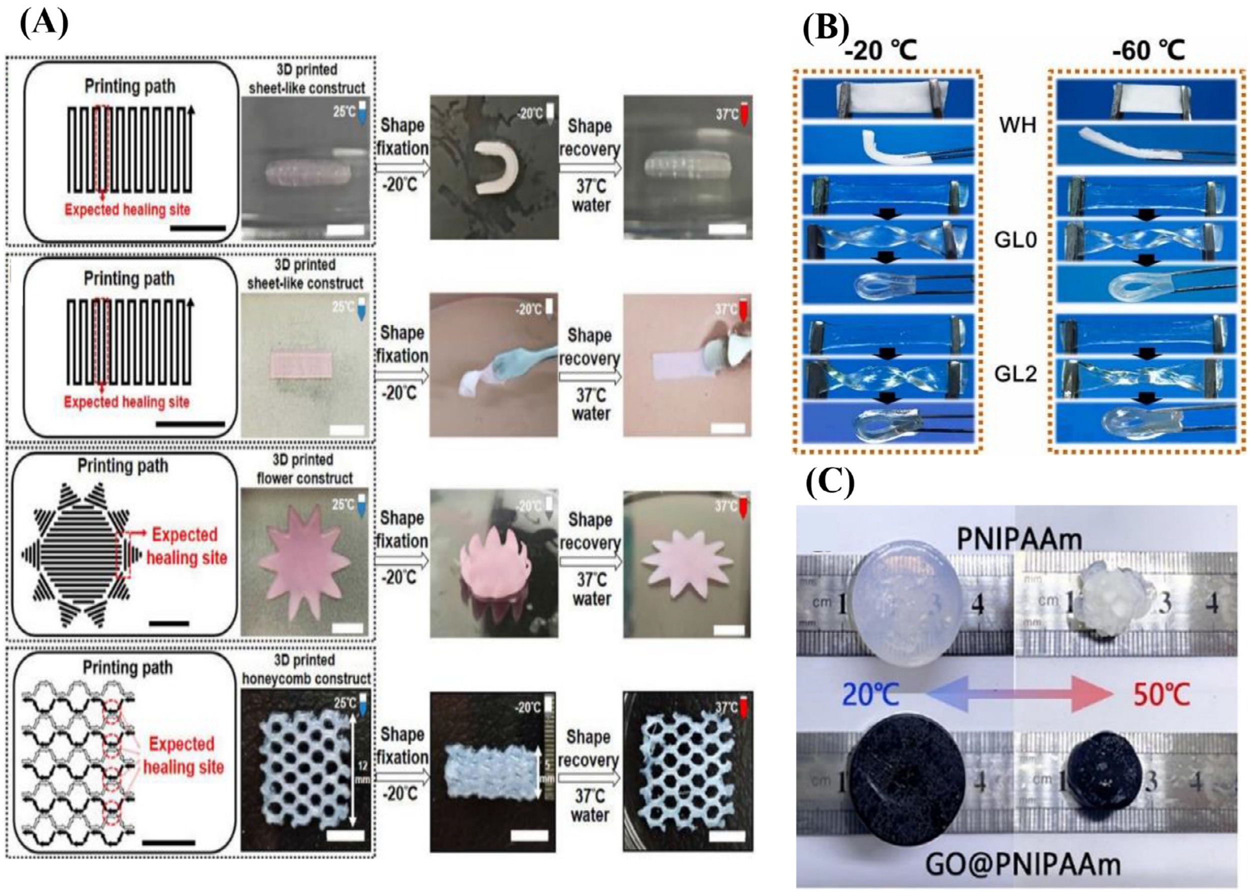


Fig. 8

(A) Shape memory and self-healing properties of the various 3D-printed PU/GelMA hydrogel including sheet-like (seven layers), flower (four layers), and honeycomb (four layers) constructs (adapted from ref. [302] copyright 2021 IOP Publishing); (B) PAM/PAA hydrogel the mechanical deformation behaviors for a week at − 20 °C and − 60 °C with various glycerol concentration (assigned as GLO-GL2 and without glycerol and LSNs, assigned as WH) (adapted with permission from ref. [303] copyright 2022 Elsevier B.V.); (C) Shape changing behavior of PNIPAM and PNIPAM/GO hydrogels before and after heating (adapted with permission from ref. [304] copyright 2022 Elsevier B.V.).

stimuli such as electric and magnetic fields [295]. Furthermore, the novel multifunctional magnetic-based smart materials through 4D printing are explored extensively today and are considered an active research topic for many researchers. For instance, Wu et al. [296] studied magnetism-responsive slanted micropillar arrays (MSMAs) for on-demand manipulation of multiple droplets using PDMS. Results showed various droplet's motion modes such as pinned, unidirectional, and bidirectional were tunable by changing the speed of the magnetic field and the volume of droplets. The bending angle of micropillars and rapid movement of droplets (10–80 mm/s) were reversibly adjusted under the action of a magnetic field. Furthermore, the liquid-involved light, electric switch, and biomedical detection were designed by manipulating the droplets on-demand as presented in Fig. 7(A). Thus, making MSMAs are promising for microfluidic and biomedical engineering applications.

2.3 3D printing of temperature-responsive hydrogels

Temperature SRHs have gained immense attention over the years due to their fast, and highly controllable response [297] for less chemical residue and higher biosafety [298]. For instance, thermo-sensitive valves based on n-isopropylacrylamide hydrogels are highly efficient for controlling the flow of fluid in micro-pumps [299]. Therefore, with the exploration of various biomaterials as well as novel nanomaterials, the versatility and high-performance in the form of multi-functionality and self-healing characteristics of hydrogels are now commonly observed [300,301]. For example, Wu et al. [302] developed a 3D-printed PU/gelatin-based self-healing hydrogel. The proposed hydrogel had outstanding photo-/thermo-responsive behavior with shape fixity (~95%) and shape recovery (~98%) during the forming and collapsing of water lattice in the hydrogel. Also, these 4D bioprinted hydrogels have cryopreserved (−20 °C or −80 °C) after awakening and shape recovery at 37 °C, as presented in Fig. 8(A), thus, potential to use in tailored biofabrication for various biomedical applications. In another study by Huang et al. [303], nanocomposites hydrogels using polyacrylamide/polyacrylic acid (PAM/PAA) with lignin sulfonate nanorods (LSNs) in water/glycerol solvent system were explored. These novel hydrogels with lignin exhibited good UV blocking performance and mechanical properties. Also, such nanocomposite hydrogels with glycerol exhibited remarkable behavior at various low temperatures such as −60 °C and −20 °C

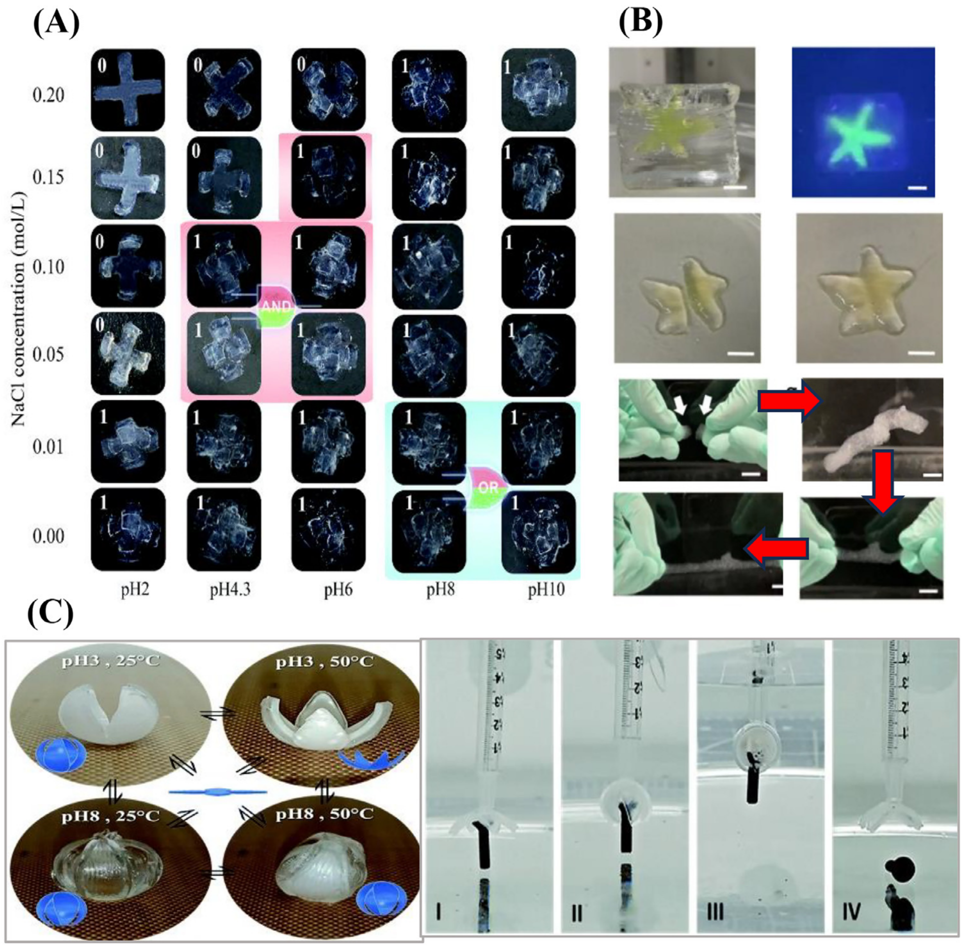


Fig. 9

(A) Various shape changing behavior of PDMS hydrogel under the effect of various NaCl concentrations and pH (the "0″ or "1″ at the upper-left corner of the images represents the output of the gripper in the form of AND gate and OR gate respectively (adapted from ref. [306] copyright 2022 Royal Society of Chemistry (RSC)); (B) Illustration of 3D Printing and self-healing behavior (under water) of KGM-Borax ink (adapted from ref. [307] copyright ©2022, Mary Ann Liebert, Inc.); (C) Dual-responsive actuation behavior under temperature and pH stimulus of a 3D-printed hydrogel in gradient-like structure, AND Grabbing (I–II–III) and releasing (IV) objects of printed structures under thermal and pH stimulus (adapted from ref. [308] copyright 2019 Royal Society of Chemistry (RSC)).

for a week without freezing as presented in Fig. 8(B). According to Gao et al. [304] temperature responsive graphene oxide (GO) improved poly(N-isopropylacrylamide) (PNIPAM) hydrogels are promising materials for the wound dressing applications. Gao and co-authors demonstrated that compression strength of hybrid hydrogels 49 times higher than PNIPAM and hybrid hydrogels are highly tunable to the transition temperature (32.7 °C to 34.8 °C), as depicted in Fig. 8(C).

2.4 3D printing of pH-responsive hydrogels

3D-printed hydrogels triggered under pH stimulus are considered a viable technology for fabricating live/dynamic structures, particularly for soft grippers and small actuators [305]. For instance, Zhang et al. [306] studied SRHs for small-scale soft grippers by preparing a pre-designed four-arm shaped well which was attached to Ecoflex mold. Zhang and co-authors demonstrated that SRH grippers captured logical output information corresponding to logic gates autonomously (AND or OR gate) triggered from expansion or contraction under various stimuli. As such, one of these responses for soft grippers under NaCl and pH variations is presented in Fig. 9(A). The proposed approach is very promising for controlling the motions of small-scale soft robots and machines in a stimulant environment.

Digumarti et al. [307] studied 3D-printed Konjac glucomannan (KGM)/Borax-based hydrogels having self-healing and pH-responsive characteristics for soft robotic applications as depicted in Fig. 9(B). Reported results showed that KGM-Borax had self-healing efficiency (98%) underwater. Thus, 3D-printed KGM/Borax-based hydrogels are ideal for the next generation of soft robots capable of reacting to various environmental stimuli and have good resilience against damage.

Odent et al. [308] fabricated anisotropy-encoded poly(N-isopropylacrylamide), PNIPAM, and poly(2-carboxyethylacrylate), and PCEA hydrogel actuators through SLA-based 3D printing. Results demonstrated that multi-responsive hydrogel-based actuators had repeatable and fast shape-changing behaviors. Furthermore, temperature and pH-based stimulus revealed continuous bidirectional bending of soft actuators and it is a promising platform for releasing and grasping various objects as highlighted in Fig. 9(C).

2.5 3D printing of humidity-responsive hydrogels

Water/humidity-responsive stimulus is considered a fundamental stimulus for producing a simple form of shape morphing behavior in the form of swelling and deswellingby absorbing water vapor and evaporating water vapors, respectively [309]. This complex behavior is attributed towards the cross-linking density of a hydrogel which produces lower volumetric expansion when the cross-linking density is high [310]. Also, the unique combination of advanced additive manufacturing technologies with water responsive hydrogels are recognized as a milestone technology for achieving highly complex, programmable, and controllable objects with intricate geometries. In this regard, PNIPAM, PEGDA, poly(acrylamide) (PAAm), poly(butyl methacrylate), PAA are well studied and documented through 3D printing for producing novel shape generation which is now in high demand [311–313]. For instance, Yang et al. [314] proposed a controllable method for humidity-responsive programmable deformation of PEGDA hydrogel structures through a single-material printing. Results showed that changes in the water absorption and swelling properties of PEGDA hydrogels, and controlled bending deformation of their structures were achieved as highlighted in Fig. 10(A_1). Furthermore, a micro-manipulator as presented in Fig. 10(A_2) successfully grasped and released tiny objects sized in centimeters or even millimeters. Thus, the proposed design offers a unique idea for micro-robots effectively used in tissue engineering and drug delivery applications.

He et al. [315] fabricated a series of hydrogels through the DLP technique. Results demonstrated that printed materials have high sensitivity under both stretching and compressive deformations. Furthermore, the dehydration behaviors of hydrogels in ethanol and the water-activated were excellent (referring to Fig. 10(B)), which are considered effective in their storage and related biomedical applications. Levin et al. [316] investigated the 3D-printing technique for characterizing the heterogeneous deformations under swelling of water beads hydrogel structures for two types of geometric confinements as presented in Fig. 10(C). The results showed transverse stretches increase by decreasing the longitudinal deformations. These interesting results can be useful for optimizing the performance of swelling for various purposes such as water-responsive hydrogels as well as for other stimuli such as temperature and pH.

2.6 3D printing of solvent-responsive hydrogels

As early as 2005, the solvent-induced recovery process was first reported. Since then it has attracted the attention of the scientific community [317]. Solvent-responsive hydrogels allow for change of the shapes of hydrogel structures and recovery from a fixed shape to a temporary shape under organic or inorganic solvent stimulus. Particularly ethanol, citric acid, and acetone are widely explored as possible solvent stimulants. The complex shape morphing behavior of the hydrogel system further improves when intricate design structures are driven by 3D printing techniques. Unlike the traditional responsive stimulus, solvent-responsive hydrogels have unique advantages for the plethora of functionalities thanks to printed hydrogel structures [318,319], thus allowing them to be used in numerous applications ranging from tissue engineering to soft robotics. Recently, Cao et al. [320] investigated thermo-responsive polycaprolactone dimethacrylate (PCLDMA) and ionic responsive sodium alginate methacrylate (SAMA) for developing self-rolling bilayer film. DIW-based 3D printing is used for fabricating complex structures (Fig. 11(A)). Results showed that when exposed to warm water and Ca^{2+} solution, the printed bilayer exhibited controllable self-rolling behavior. In addition, the biomaterials employed in the proposed 4D printing technique are highly promising as vascular stents.

The organic solvent can produce a reversible dilating mechanism and contract polymer matrix allowing structures to achieve more complex and advanced shape-morphing behavior. For instance, Parimita et al. [319] prepared chitosan (CS)/citric acid (CA)-based hydrogel through DIW 3D printing demonstrating excellent shape-morphing properties under an external trigger stimulus ethanol as presented in Fig. 11(B_1). Furthermore, different complex 3D architectures were printed and modified by trimethyl silane (TMS) hydrophobic coating. The shape-morphing CS/CA hydrogel through 3D printing has numerous applications in actuators, and grippers, for soft robotics as it lifts an object seven times its weight as highlighted in Fig. 11(B_2). In another novel study by Lei et al. [321] "shapeability" of various stimulant responsive hydrogel inks in different support baths including agarose fluid gel gelatin slurry, oil-based, carbopol baths have been explored. The insights from this work demonstrated that oil support baths as presented in Fig. 11(C) inhibited all transport events and reduced interfacial tension at the ink–bath interface. This novel embedded 3D printing for stimuli-responsive hydrogels is a promising platform for producing architected soft for numerous applications in tissue engineering.

2.7 3D printing of light-responsive hydrogels

The excessive availability of UV radiation and their exposure through naturally available sources such as the sun as well as some artificially created in the form of near-infrared-light (NIR) have significant advantages [322]. For example, UV light is an inexpensive technology, easy for various high-end engineering applications in sensors, actuators and humans as well [323]. This approach combined with 3D printing has now widened the spectrum of hydrogel materials to enable rapid, affordable, and easy to regulate the shape-morphing behavior for multiple intriguing structures. Recently, Yang et al. [324] investigated a bio-inspired micro-propeller robot using PNIPAM/CNTs, and magnetic materials through extrusion-based 3D printing techniques under magnetic and optical coupling field stimulus. Results showed that the hydrogel under light stimulus produced a recoverable and controlled deformation for micro-robotic structures such as the swimming of a bionic jellyfish, as highlighted in Fig. 12(A). Furthermore, the bio-inspired propeller demonstrated complex degrees of freedom for motion along with their ability to carry objects in a microfluidic environment under optical and magnetic coupled fields. It was envisioned that the proposed methodology would be useful for navigators in liquid environments.

Zhao et al. [325] developed stimuli-responsive graphene oxide (GO)/nanoclay/PNIPAM-based hydrogels using extrusion-based 3D printing. Moreover, PNIPAM precursors were treated silane

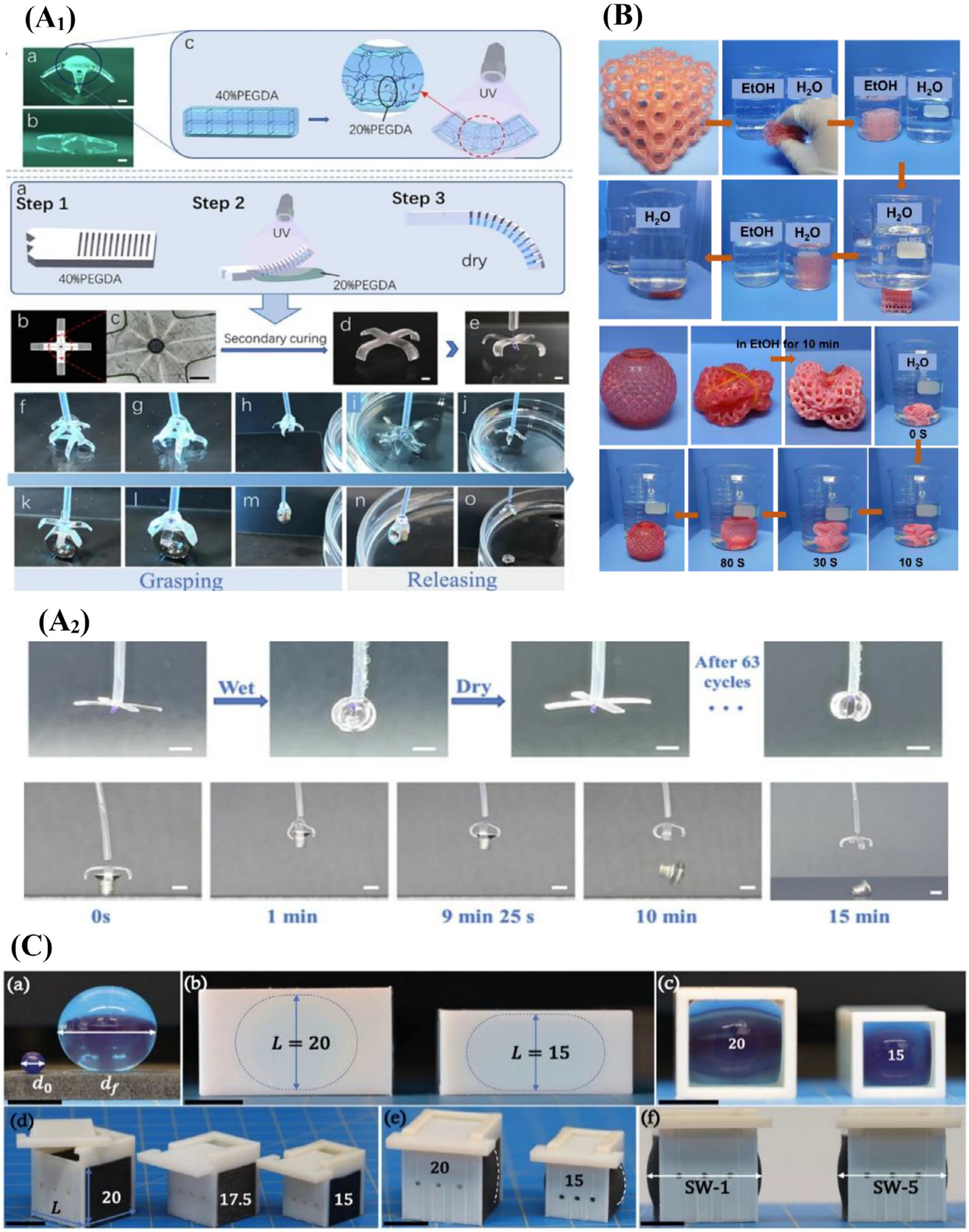


Fig. 10

(A_1) low concentration hydrogel solution deformation under mode I driven by unilaterally absorbing the prepolymer solution and curing internally, and the skeletonized structure of the hydrogel showing deformation under mode II for developing micro-manipulator for grasping and releasing of objects in control manner, (A_2) Performance of the micromanipulator demonstrating its gripping and releasing behavior (adapted with permission from ref. [314] copyright 2022 Elsevier Ltd.); (B) Dehydration of the hydrogel in ethanol and water-activated shape memory property of the hydrogel (adapted from ref. [315] copyright 2021 American Chemical Society); (C) Comparison of dry and a freely-swollen water bead hydrogel (99% water) in various in the form of transversely constraining and elastically constraining boxes (adapted with permission from ref. [316] under the terms of the Creative Commons Attribution license 4.0.).

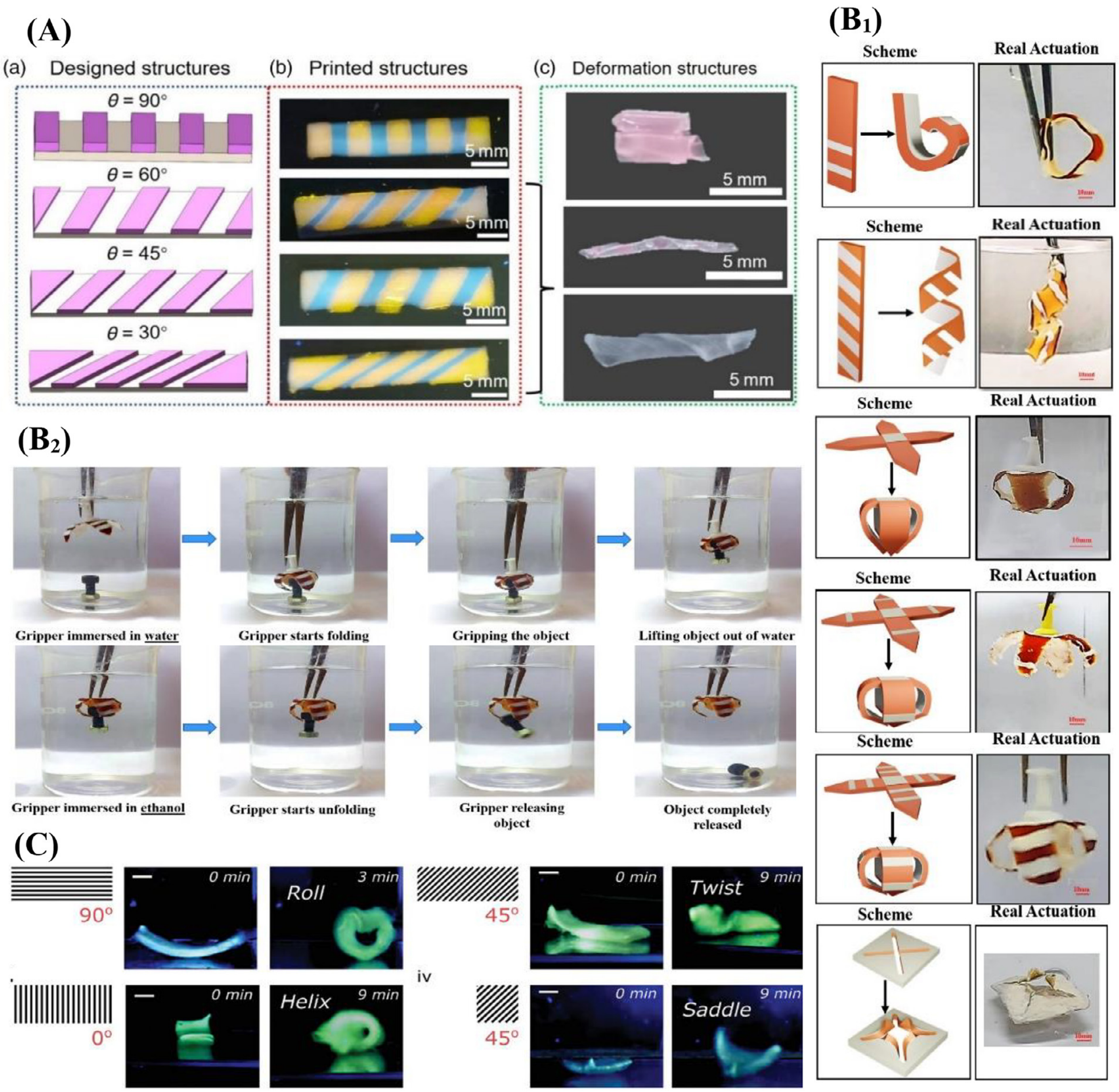


Fig. 11

(A) (a) Designed structures of the bilayer film with various patterns, (b) snapshots of the 4D printed various bilayers under UV light, (c) printed bilayer films self-rolled behavior under Ca^{2+} solution (adapted from ref. [320] copyright 2022 Wiley Periodicals LLC.); (B_1) Various 4D-printed CS structure coated with silane stimulus, (B_2) Images of a soft gripper illustrating grasping and releasing of an object (adapted with permission from ref. [319] copyright 2022 The Society of Manufacturing Engineers. Published by Elsevier Ltd.); (C) Various soft morphing systems produced in an oil-based bath via embedded printing (adapted with permission from ref. [321] under the terms of the Creative Commons Attribution license 4.0.).

with prescribed shapes and spatial control. Excellent shape morphing behavior was demonstrated as presented in Fig. 12(B) by the nanocomposites under UV light and temperature. Folding and bending to occur for non-swellable decellularized leaf find promising applications in biosensors and soft actuators.

Shao et al. [326] studied photo-responsive graphene and silicon rubber/PDMS-based bilayer structure through 3D printing. The developed 3D-printed composite exhibited tunable optically responsive motions such as bending, grasping, and crawling and self-sensing characteristics, as highlighted in Fig. 12(C_1)-Fig. 12(C_2). This was achieved during the proof concept demonstration of the muscle-like actuator under light-driven programmed locomotion for promising applications expected in soft robotics.

Zhang et al. [327] prepared self-assembled PNIPAM/GO nanocomposite hydrogel through three-dimensional printing. GO further improves fast photo-thermal infrared light absorber capacity in the form of shrinkage and swelling by controlling NIR light on or off. Moreover, a 3D-printed round-tube nanocomposite hydrogel was successfully employed as a pencil for potential use as an actuator as presented in Fig. 12(D).

Chen et al. [328] explored highly flexible and stretchable (1500%) PDMS hydrogel through DLP using a novel PμSL printer. The insight of this study showed that highly tunable and optical

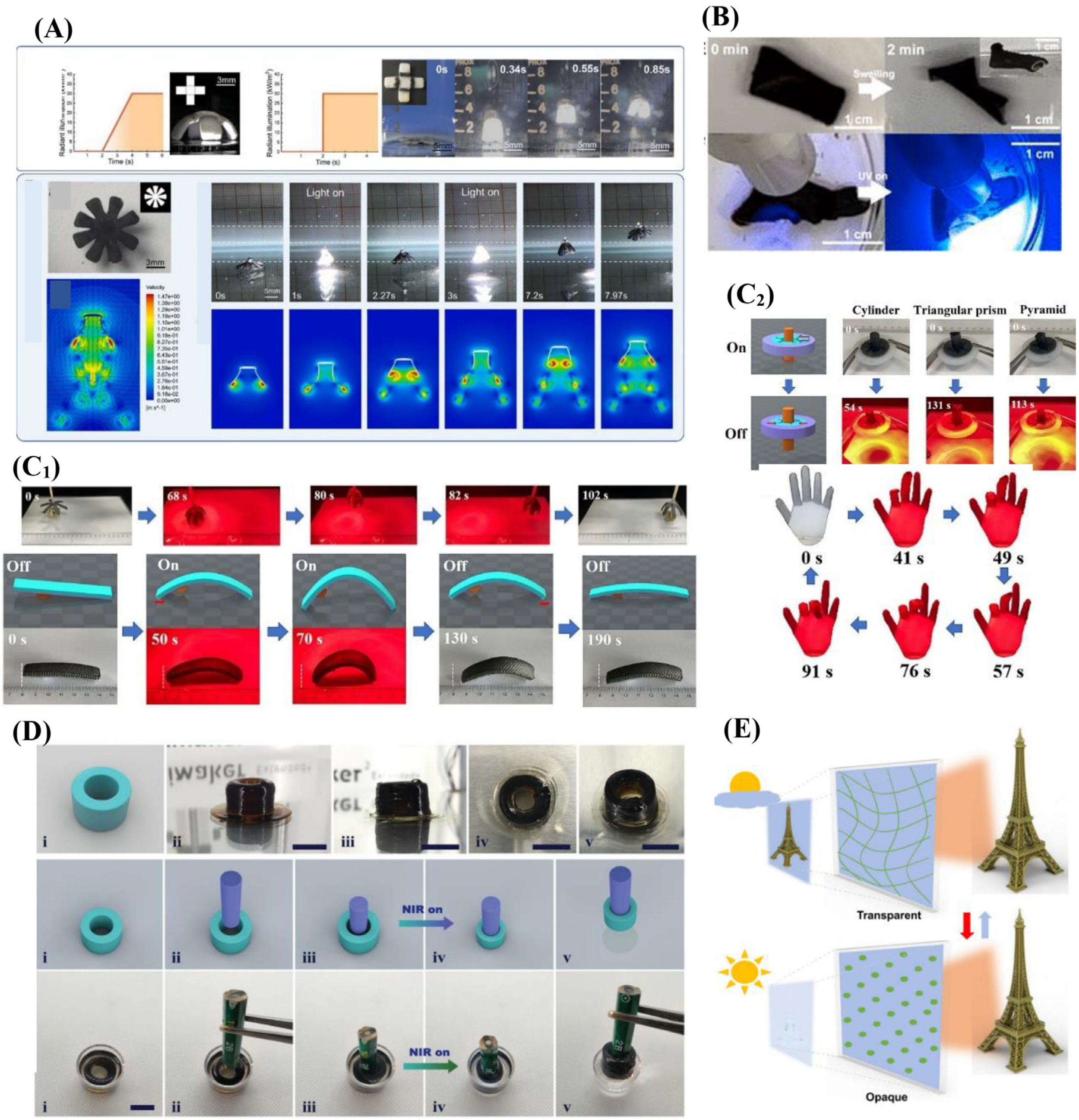


Fig. 12

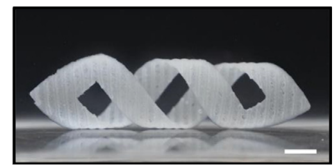
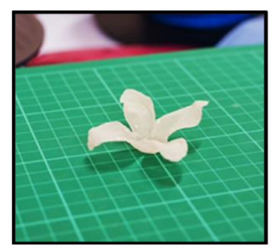
(A) Image of "+" shaped hydrogel with locally dipped CNTs and its light response behavior standing and jumping standing action under increased light intensity, and finite element analysis and actual images of light-driven swimming of a bionic jellyfish (adapted with permission from ref. [324] copyright 2023 Elsevier B.V.); (B) Swelling type shape morphing behavior of the bilayer structure silane-treated decellularized leaf (GO/nanoclay/PNIPAM hydrogels) at 22 °C, and deswelling behavior under UV irradiation (~1 W/cm^2) (adapted from ref. [325] copyright 2022 American Chemical Society); (C_1) Asterisk-shaped (*) printed gripper used for transporting a quail egg, and bionic hand in response through its various shape-deformation behaviors under NIR irradiation, (C_2) The grabbing of different objects through 3D-printed the triangular prism, cylinder, and pyramid objects through double-wall ring-shaped gripper, and crawling robot crawls during NIR irradiation on and off (adapted with permission from ref. [326] copyright 2022 Elsevier B.V.); (D) The model and various images of the hydrogel 3D structure, Schematic and real-time illustration of grabbing mechanism of an object with a small size than tube during the NIR laser irradiation (adapted from ref. [327] copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (E) Conceptual design of smart window concepts and its proposed mechanisms under thermo-light responsive hydrogel (adapted with permission from ref. [328] under the terms of the Creative Commons Attribution license 3.0.).

performance was observed for the next generation of soft smart windows as presented in Fig. 12(E). Also, PDMS hydrogel showed transparent-opaque transition with high solar modulation up to 79.332% near its lower critical solution temperature.

Thus, 3D-printed SRHs have been extensively applied to develop smart structures for different engineering applications. Table 3 summarizes some of the recent structures developed by researchers using the combination of SRHs and 3D printing.

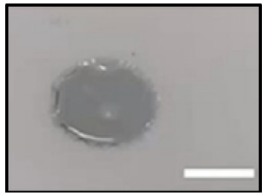
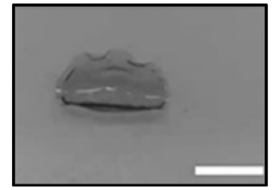
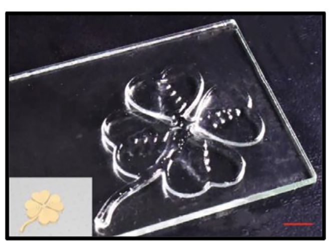
Table 3

A review of recent stimuli responsive behavior of 3D-printed hydrogels for exciting applications.

3D printing process	Smart hydrogels	Printed 2D model(s)	Stimulus	Stimulated 3D model(s)	Applications	Ref.
Extrusion-based printing	Alginate/ methylcellulose		Deionized water		Soft robotics	[329]
Extrusion-based printing	PNIPAM/PANI		Temperature		Flexible electronics	[330]
FDM	CMC		Water		Complex architectures and actuating structures	[331]

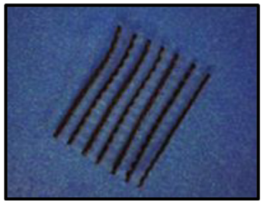
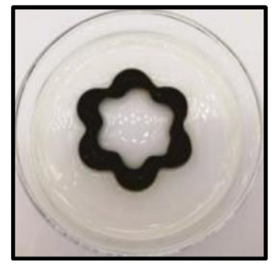
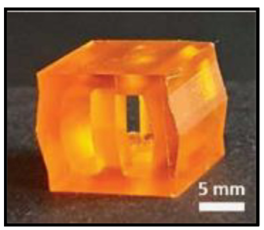
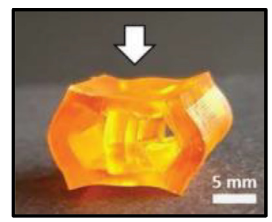
(*continued on next page*)

Table 3 (*continued*)

3D printing process	Smart hydrogels	Printed 2D model(s)	Stimulus	Stimulated 3D model(s)	Applications	Ref.
DIW	AA-MA		Ions		Vascular stents	[332]
DIW	MC/alginate/PAA/Fe_3O_4		Magnetic field		Tissue scaffolds	[333]
DIW	PNIPAM/clay		Temperature		Bionic grippers	[334]
DIW	PNIPAM/PAAM		Temperature		Multifunctional biomedical devices	[335]

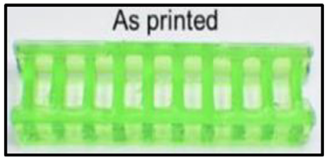
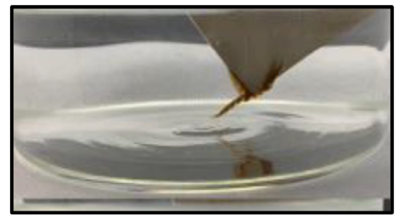
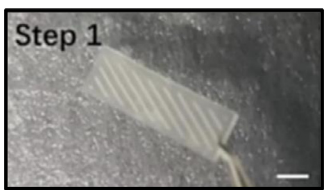
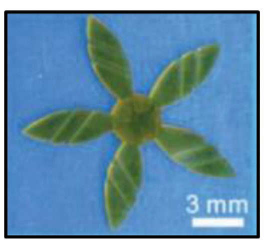
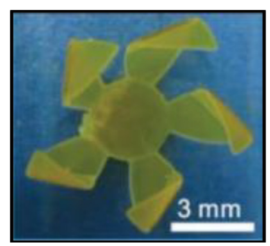
(*continued on next page*)

Table 3 (*continued*)

3D printing process	Smart hydrogels	Printed 2D model(s)	Stimulus	Stimulated 3D model(s)	Applications	Ref.
DIW	PNIPAM/ PEGDA/Fe_3O_4		Solvent and magnetic field		Soft robotics	[336]
DIW	GO/PVA		pH and enzymes		Controlled drug delivery and tissue engineering	[337]
DLP	PEGDA		Temperature		Smart lattice structures	[338]
DLP	PNIPAM		Temperature		Tissue Engineering	[339]

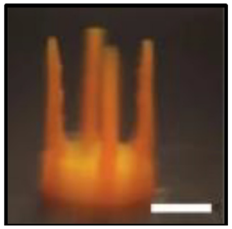
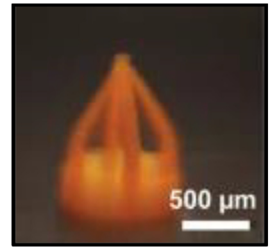
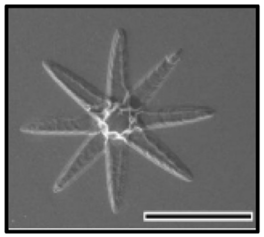
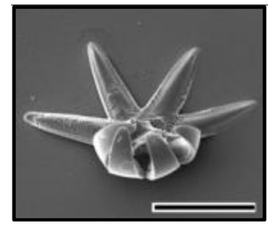
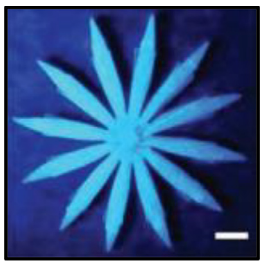
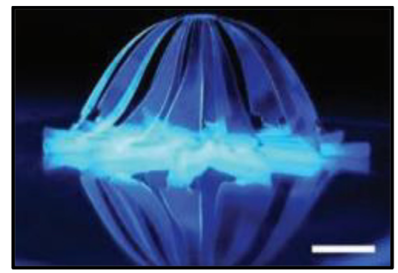
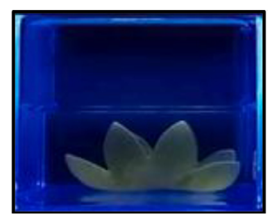
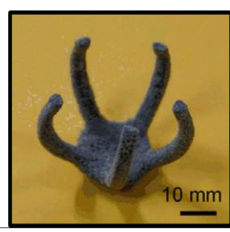
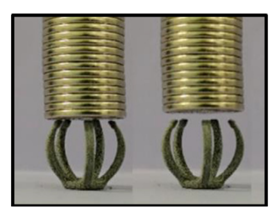
(*continued on next page*)

Table 3 (*continued*)

3D printing process	Smart hydrogels	Printed 2D model(s)	Stimulus	Stimulated 3D model(s)	Applications	Ref.
DLP	PEGDA		Temperature		Lattice structures	[340]
DLP	PEGDA/iron particles		Magnetic field		Smart actuators	[287]
DLP	PEGDA		Water		Micro/nano-scaled grippers	[314]
SLA	PEGDA		Temperature		Scaffolds and smart actuators	[202]

(*continued on next page*)

Table 3 (*continued*)

3D printing process	Smart hydrogels	Printed 2D model(s)	Stimulus	Stimulated 3D model(s)	Applications	Ref.
μSLA	PNIPAM		Temperature		Biomedical devices	[341]
TPP	PEGDA/HAMA		Temperature		Soft grippers	[342]
TPP	PNIPAM		Temperature		Biomedical devices and artificial limbs	[343]
Vat polymerization	PNIPAM/AA		Light		Soft robots, data security protections, and implantable sensors	[344]
SLS	TPU/Nd2Fe14B		Magnetic field		Smart grippers	[92]

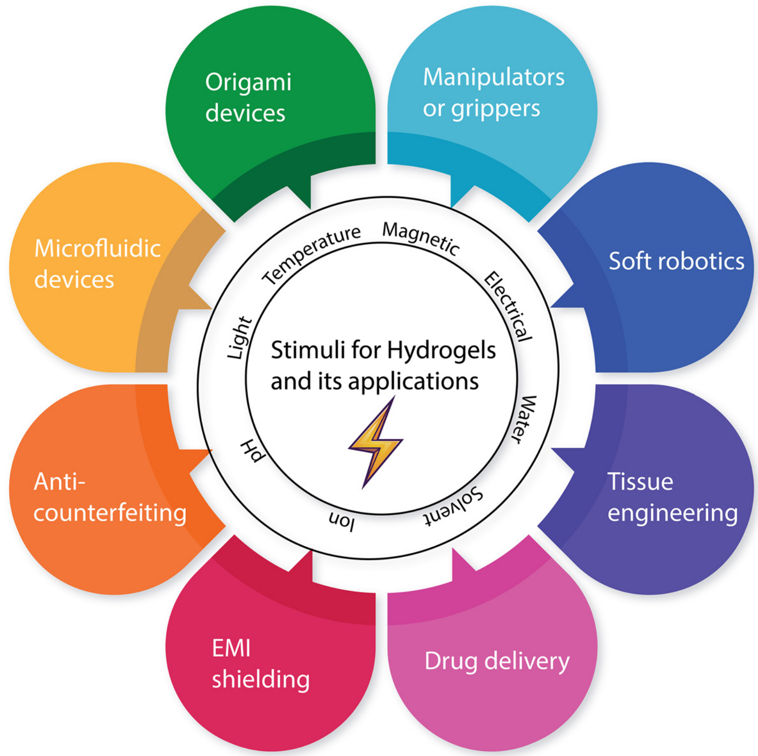


Fig. 13

Versatile applications of 3D-printed SRHs.

3 Emerging applications of 3D-printed SRHs

Hydrogels under any stimulus show large volume changes which are performed by actuation movements in two ways. First, anisotropic stimuli are required for a homogeneous hydrogel structure. Second, homogeneous stimuli are needed for an anisotropic hydrogel structure and this approach is more effective [345–347]. 3D printing is convenient for producing anisotropic hydrogel structures for tissue engineering and controlled drug delivery applications [348–351]. This section also covers the recent developments in terms of shape-morphing behavior such as self-assembly, self-healing, and changes in various material properties, which are responsible for their advanced applications in various sectors [352–358]. Table 4 incorporates the recent hydrogel-based smart structures developed by using different 3D printing techniques and their deformation mechanisms. Fig. 13 highlights the applications of 3D printing of SRHs in various domains.

3.1 Soft robotics

Soft robotic is continuously gaining significant attention ranging from academia to industrial sectors for their unique role in various exciting applications in sensors and actuators as well as tissue engineering [402–404]. Soft robotics has the ability to respond under multiple actuation mechanisms that are appealing to develop highly flexible and adaptable sensors in any complex environment. Inspired by natural organisms, soft robotics have been designed to achieve highly elastic, motorless-driven mechanisms, deformable, and remarkable shape-morphing behavior in comparison to their rigid counterparts [405–407]. 3D-printed soft robot made from soft polymeric materials such as hydrogels further improves their characteristics, especially in narrow spaces and complex environments where human interaction is not possible by offering a high degree of freedom in the form of bending, rolling, twisting and folding [326]. Moreover, these soft robots are now successfully employed in minimally invasive surgery by offering various flourishing tools such as magnified 3D vision, highly dexterous surgical equipment, and highly-intuitive human-robot interfaces for precisely controlling tool motion, thus, improving overall surgeon capabilities [408].

For instance, Sun et al. [409] fabricated marine-sourced hydraulic actuators using fresh calcium-alginate hydrogels by printing thin-wall water-tight and pressurizable structures. Results confirmed that actuators had various features such as complex shapes and internal cavities with safely edible, biodegradable, and digestible by marine organisms. Finally, marine robot demonstrated its complex soft-device aspects such as transporting various objects as presented in Fig. 14(A). In another study, Tetsuka et al. [410] multi-layer printed various micropatterns of hierarchical and multilayered scaffold techniques using PEG/GelMA with a pattern of the hard PEG/GelMA perpendicular orientated. Results showed that the sarcomeric longitudinal muscle layout guides the actuation dynamics parallel to the CNT/GelMA hydrogel lines for exhibiting soft robotic motion during an upward contraction, as presented in Fig. 14(B).

Yang et al. [411] investigated microfluidic 3D droplet printing for composite elastomers. The printed composite elastomers demonstrated excellent multi-shape (bow- and S-shaped), multistep (one- and two-step), and multimode (gradual and sudden), in response to different stimuli such as

Table 4

A summary of recent works about the 3D printing of SRHs developed for different engineering applications

Stimuli	3D printing	SRHs	Shape change deformation mechanisms/programming	Applications	Ref.
Temperature	Extrusion	PNIPAM	Sequential shape change	Drug delivery device	[359]
Temperature	Extrusion	PCLA-PEG-PCLA/CNC	Bending	Tissue scaffolds	[360]
Temperature	DIW	PNIPAM/CNC	Functional property change	Biomedical applications	[361]
Temperature	DIW	AA/CNC	Self-healing	Wearable sensors	[362]
Temperature	Extrusion	PDMA/n-octadecyl acrylate	Bending	Skin-like sensors	[363]
Temperature	Extrusion	GelMA/rGO	Bending	Bone tissue scaffolds	[364]
Temperature	DLP	PEGDMA	Folding	Microfluidic devices	[365]
Temperature	SLA	Chitosan/PEGDMA/CNF	Folding	Tissue scaffolds	[366]
Temperature	TPP	PNIPAM	Folding and unfolding	Energy consumption systems	[367]
Temperature	TPP	PNIPAM	Folding and rolling	Bionic soft micro-robots	[368]
Temperature	μSLA	PNIPAM	Bending	Soft robots	[341]
Temperature	DIW	PNIPAM/PEGDA/alginate	Rolling	Hollow tubes for biomedical applications	[369]
Temperature + ions	DIW	SAMA/PCLDMA	Self-rolling	Vascular stent	[320]
NIR light	Extrusion	Gelatin/β-TCP/SC	Shrinking	Bone cancer treatment	[370]
NIR light	DIW	PDA/PCL	Shrinking and bending	Localized cancer therapy and wound healing	[371]
NIR light	μSLA	PNIPAM/PEGDA/AA	Bending	Micro-robots	[372]
NIR light + magnetic field	DIW	PNIPAM/PEG/Fe_3O_4	Shrinking, swelling, and flipping	Soft carriers	[373]
Light + electricity	DLP	PNIPAM/graphene	Folding	Intelligent soft actuators	[374]
Light + solution	Extrusion	AAm-AAc/CNC	Bending and stretching	Clinical applications	[375]
Light + humidity + temperature	TPP	PEGDA/HAMA	Shrinking, swelling, and bending	Soft micro-grippers	[342]
Humidity	DIW	PNIPAM/CNC	Bending, twisting, and swelling	Self-supporting complex structures	[376]
Humidity	Extrusion	Agar/soy-protein	Swelling	Tissue scaffolds	[377]
Humidity	DLP	PEGDMA	Swelling and bending	Bionic structures	[314]
Humidity	DLP	GelMA/PEGDMA	Swelling	Tissue scaffolds	[378]
Humidity	DLW	PEGDA/EPOX/Silver particles	Swelling	3D cross-shape pattern	[379]
Water	DIW	GelMA/CNC	Contraction and swelling	Smart actuators	[380]
Water	Extrusion	AA-MA and HA-MA	Self-folding	Tissue vascularization	[381]
Humidity	FDM	PU/elastomer	Folding and twisting	Origami structures	[382]
Magnetic field	DIW	Fe_3O_4/PNIPAM	Stretching and bending	Hyperthermia cancer therapy	[383]
Magnetic field	TPP	GelMA/Fe_3O_4	Bending and folding	Micro-robots	[384]
Magnetic field	TPP	GelMA/Fe_3O_4	Folding, bending, and gripping	Milli-grippers	[385]
Magnetic field	μSLA	Alginate/Mn/CoNiP-based layer	Folding and unfolding	Micro-devices for drug delivery	[386]
Magnetic field	DLP	PEGDA/MNPs	–	Anti-counterfeiting applications	[387]
Magnetic field	DLP	Iron particles/PEGDA	Folding and bending	Magnetic actuators and soft robotics	[287]
Magnetic field	DIW	Alginate/methylcellulose/ PAA	Rolling, jumping, and bending	Smart actuator	[242]
Magnetic field	Extrusion	Gelatin/carrageenan/Fe_3O_4	Rolling	Intelligent cargo and drug delivery	[388]
Magnetic field + temperature	Vat photo-polymerization	PNIPAM/ laponite nanoclay/NdFeB	Folding and bending	Soft millirobots	[389]
Electric field	DIW	PEGDA/AA	Bending	Soft actuators	[390]
Electric field	DLP	PAA	Gripping and folding	Soft robot	[391]
Electric field + magnetic field	DIW	Chitosan/Fe_3O_4	Bending and gripping	Untethered milli-gripper	[392]
Electric + temperature	Extrusion	κ- and ι-carrageenan	Swelling and shrinking	Controlled release systems	[393]
pH	DLP	PEGDA/AA	Swelling and shrinking	Controlled drug delivery device	[394]
pH	Extrusion	CMCS/CNC/DOX	Swelling	Controlled drug delivery for cancer treatment	[395]
pH	TPP	PEGDA	Swelling	Bio-sensors	[396]
pH	FDM	Peptide	Self-assembly	Oral delivery for gastrointestinal tract treatment	[397]
pH	SLA	PEGDA/HEMA/TPO/AA	Swelling and shrinking	Smart wound dressings	[398]
pH	μSLA	AA/PEGDMA	Shrinking and swelling	Tissue scaffolds	[399]
pH + osmotic pressure + temperature	SLA	PNIPAM	Swelling and bending	Smart actuators	[308]
pH + ions + magnetic field + temperature	TPP	PNIPAM/AA	Swelling and shrinking	Mobile micro-machines	[400]
Ions	DIW	AA-MA	Swelling and shrinking	Vascular stents	[332]
Solvent	DIW	Chitosan/citric acid	Bending	Soft robots and actuators	[319]
Solvent	DLP	PUA/acrylamide/AA	Stretching and compression	Soft lattice structures	[315]
Solvent	Extrusion	Alginate/methylcellulose	Swelling	Soft robots	[329]
Solvent + temperature	DIW	PU/CMCS/carbomer	Swelling	Intelligent robotics and bionic prosthetics	[401]

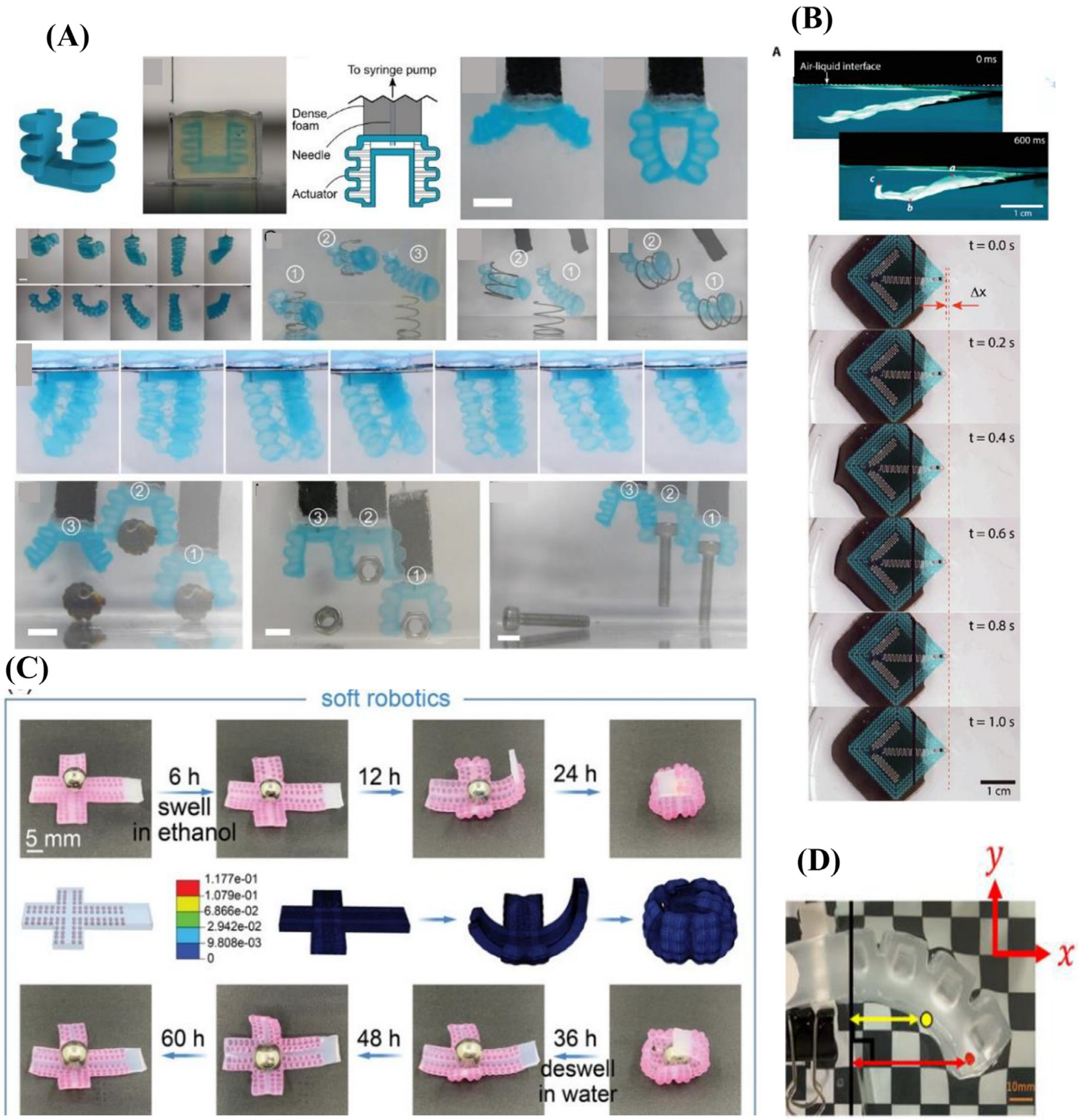


Fig. 14

(A) CAD and actual images of the 3D-printed soft hydrogel gripper, and demonstration of the objection handling capability of FRESH-printed grippers including grabbing, moving, and releasing of various objects, including a sea snail, M3 hex nut, and M3 socket head screw (adapted with permission from ref. [409] under the terms of the Creative Commons Attribution license 4.0); (B) Actuation behaviors of biohybrid soft robots; side-angle, and various snapshots of locomotion of soft robot during the single stroke of a 1 s recording (no wireless pacing, day 7) (adapted from ref. [410] copyright 2022 Wiley-VCH GmbH); (C) Printed soft robot demonstrating its shape morphing behavior through encapsulation and release of a steel ball through deformation and recovery, respectively, with FE simulations results and experimental results (adapted from ref. [411] copyright 2023 Wiley-VCH GmbH); (D) Snapshot of measured points of 3D-printed hydrogel actuator (adapted with permission from ref. [412] under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 Licens).

temperature, solvent and light. Furthermore, droplet-embedded composite elastomers used for various systems, such as soft robots, and biomimetic flowers, and a series of functional performances, as presented in Fig. 14(C). Likewise, Takishima et al. [412] characterized a novel soft actuator through a 3D-printed hydrogel that mimics a jellyfish. The actuator parts made of hydrogels had highly elastic properties and their normalized contraction ratio was very close to the value of moon jellyfish. The reported results indicated that the 3D-printed actuator is highly promising for a jellyfish-mimic robot, as highlighted in Fig. 14(D).

3.2 Tissue engineering and drug delivery

3D-printed SRHs are flourishing due to the appealing advantages in drug delivery systems [413–416]. Recently, Chen et al. [417] designed three-chamber electromagnetic-driven peristaltic 3D-printed micro-pump suing NdFeB/polydimethylsiloxane (PDMS) film. Insightful results showed that the three-chamber valved model performance was optimized for maximum output flow and back pressure under synchronous starting conditions for advanced drug delivery systems.

Narupai et al. [418] investigated 3D-printed protein-based programmable structure made of hydrogels that can change under multi stimuli such as pH, temperature, or an enzyme. A DIW-based 3D printing was employed using PNIPAM and poly(dimethylaminoethyl methacrylate) hydrogels. Thus, protein-based hydrogels demonstrated remarkable shape changing behavior under multi stimuli, as depicted in Fig. 15(A) which are irreversibly altered by enzymatic degradation. Promising applications are expected in the control drug delivery system.

Significant progress has been made in 3D bioprinting of conductive hydrogels for producing high-resolution biomimetic structures with gradual complexity. 3D-printed hydrogels have unique characteristics such as customizable physicochemical properties, multiple sensitivities, biodegradability and exceptional biocompatibility for specific medical treatment conditions.

Dutta et al. [419] proposed DIW-based highly stable and conductive polypyrrole (PPy)-grafted GelMA structures. Excellent shear-thinning properties were achieved due to the triple-cross-linked hydrogel. Results demonstrated high-resolution biological architectures had various abilities such as self-support, high structural stability as presented in Fig. 15(B) and “plug-like non-Newtonian” flow behavior with minimal disturbance. Thus proposed work provides a reliable 3D printing strategy for the fabrication of GelMA-PPy bioink as tissue engineering applications.

Lee et al. [420] 3D-printed multifunctional pollen grain-inspired hydrogel (MPH) using iron platinum (FePt)/pentaerythritol triacrylate (PETA)/(PNIPAM)/poly(n-isopropylacrylamide acrylic acid (PNIPAM-AA). The various printed structures showed targeted functions: torque-driven surface rolling and steering under magnetic fields, on-demand surface attachment (anchoring) under temperature response, and cargo release under pH-response as depicted in Fig. 15(C). It was envisaged that this 3D-printed potential microbot would enhance projected performance and functional diversity for controlled and efficient drug delivery as well as tissue engineering applications.

3D-printed human organs capable of performing similar human functions are no longer a dream for bioengineers. But this gap is now bridged thanks to the development of 3D-printed hydrogels. Recently, bioengineered heart has been printed from DIW-based 3D printing using alginate/PVA and PNIPAM hydrogels [421]. Results of this novel study showed that the integration of a diversified hydrogel family with 3D printing under a stimulant environment renders an enriched design platform for bioengineered robotic heart capable of performing beating–transporting functions as depicted in Fig. 15(D).

A rapid orthogonal photo-reactive 3D-printing was used by Cheng et al. [422] to highlight the role of gelatin-based tough hydrogels tissue engineering. Results demonstrated 3D-printed robust hydrogel has outstanding mechanical and wear-resistance performances, as presented in Fig. 15(E). Additionally, the 3D-printed hydrogels exhibited nontoxicity biocompatibility and antibacterial properties to use as artificial meniscus scaffolds. Cao et al. [332] prepared stimulus-responsive, methacrylated alginate (AA-MA) hydrogel inks for 3D printing and demonstrated their excellent structural resolution properties by immersing the hydrogel structures in Ca^{2+}/chitosan solution. Results showed that the controllable size of the hydrogel structure was achieved due to the continuous increase of the crosslinking density of the hydrogel. This 4D-printed material has similar biocompatibility to those of sodium alginate (SA) tubular structures and thus can be used as vascular stents in biomedical applications.

3.3 Wearable electronics

The integration of many functions of actuation and sensing would be considered perfect sensing materials. 3D printing of SRHs has enormous use in many soft devices such as flexible electronics. For instance, Wu et al. [423] used poly(acrylic acid (AA)-N-vinyl-2-pyrrolidone (NVP))/CMC-based hydrogel for printing ink. Results showed that the printed hydrogel demonstrated excellent mechanical properties and self-healing characteristics such as healed stress at 81% and healed strain at 91%. Various objects like manipulators were successfully customized using these novel hydrogels by photocurable 3D printing having high toughness and complex structures and capable of performing many functions as highlighted in Fig. 16(A). Thus, 3D-printed high-performance hydrogel are promising materials such as a flexible wearable sensor. Khoshnoo et al. developed a novel 3D-printed sensor system using polydimethylsiloxane (PDMS)/silver NPs materials, for real-time pH monitoring. Results showed that the 3D-printed nanomaterials on skin-like flexible substrates enabled multilayer printing of the sensors and reusable electronic/communication circuity. Furthermore, these sensor systems demonstrated high sensitivity, mechanical flexibility, and excellent biocompatibility for several pH ranges (3.0–10.0). As shown in Fig. 16(B), the printed sensors demonstrated the pH real-time monitoring in an ex-situ hydrogel-based wound model [424].

Recently various ionotropic hydrogels have gained immense interest in fabricating a wide range of wearable devices, energy devices and flexible electronics. A novel study by Seong et al. [425] developed 3D-printed, ionotronic hydrogels through synergistic dual reversible interactions of PVA, pectin, and tannic acid (PPT). Results showed that the ionotronic hydrogels exhibited excellent intrinsic ionic conductivity, self-healing behavior and complex patterns as wearable strain sensors during real-time implementation for human motions detection as presented in Fig. 16(C_1)- Fig. 16(C_2). Thus, opening the door for various wearable healthcare biomedical applications.

3.4 Food industry

The fast-evolving plant-based food market ignites the development of stimuli responsive hydrogels [426–428]. This technology offers various advantages in terms of personalized nutrition, customized food, consumer’s criteria of taste, enhancing the functionality of essential plant-based constituents [429], texture, cost, and effective consumption of various types of food ingredients [430]. In this regard, 3D-printed hydrogels and various natural polysaccharides have been explored wildly [431]. Moreover, 3D printing technology with naturally available hydrogels is now defining new borders for the food industry. For instance, Maniglia et al. [432] investigated the dry heating treatment (DHT) effect on wheat starch to improve the printability of hydrogels inks. Promising results suggested that DHT caused the expansion of granule size without altering the shape of the starch granules as presented in Fig. 17(A). and can be used

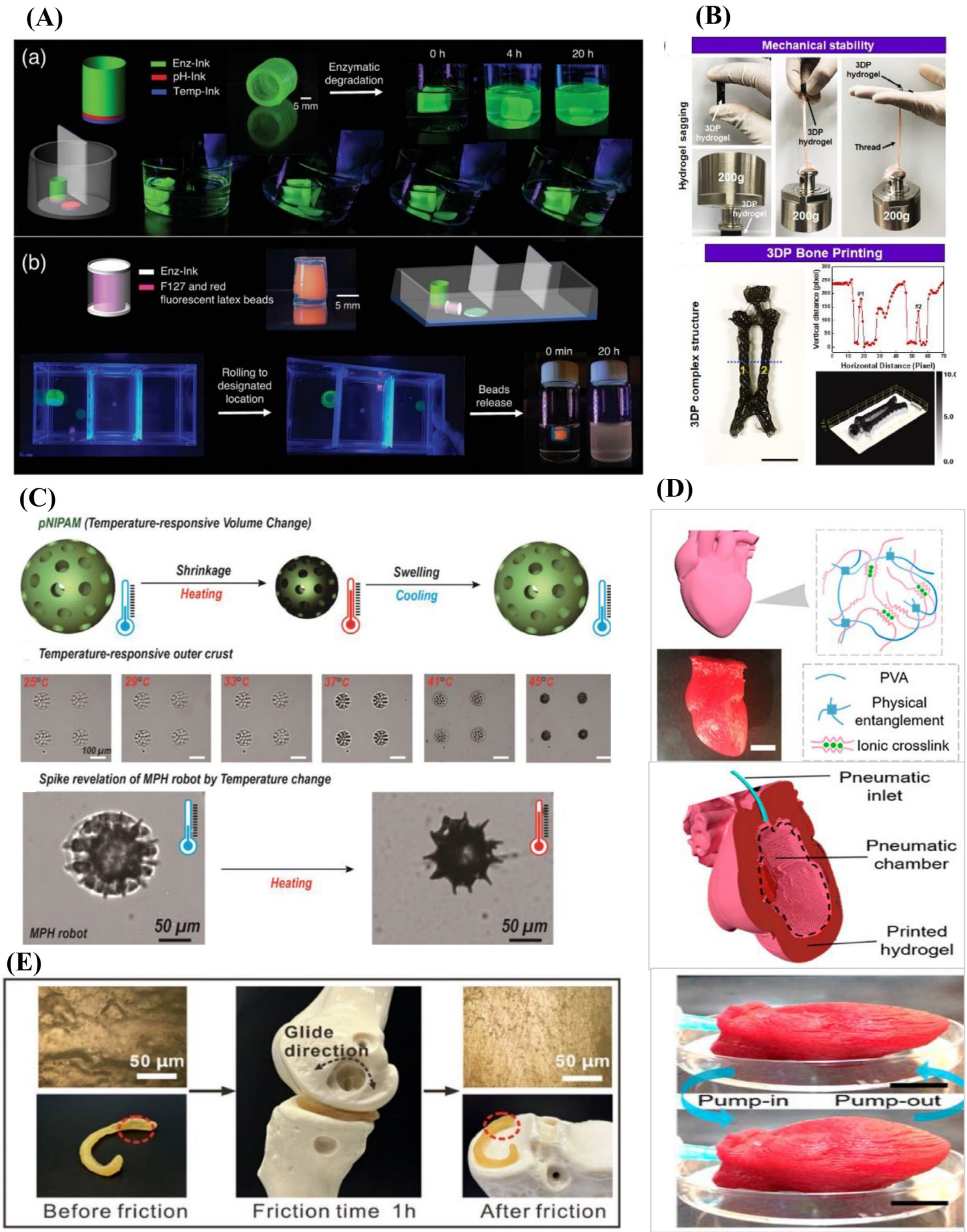


Fig. 15

(A) Cargo transport and delivery would expand their applications in broader drug delivery field (adapted from ref. [418] copyright 2021 Wiley-VCH GmbH; (B) Weight lifting study to evaluate the mechanical stability of the 3D-printed hydrogel (the 3D printing was performed using 90% infill density to maximize the mechanical performance), and demonstration of a full-length rat bone structure using GelMA-PPy ink (adapted with permission from ref. [419] copyright 2023 Elsevier Ltd.); (C) Schematic depiction of shrinkage of outer crust of MPH robot under temperature-stimulus, microscopic real-time snapshots depicting size changes for outer crust structures of PNIPAM hydrogels with changes in temperature, and optical snapshots of the MPH robot with the controlled revelation of spike structures under temperature stimulus (adapted with permission from ref. [420] under the terms of the Creative Commons Attribution license 4.0); (D) Schematic and real images for beating–transporting functions of bioengineered robotic heart, and pneumatic pumping triggers the beating of the robotic heart (adapted from ref. [421] copyright 2019 American Chemical Society); (E) Frictional test of the meniscus-like 3D-printed hydrogels (adapted with permission from ref. [422] copyright 2023 American Chemical Society).

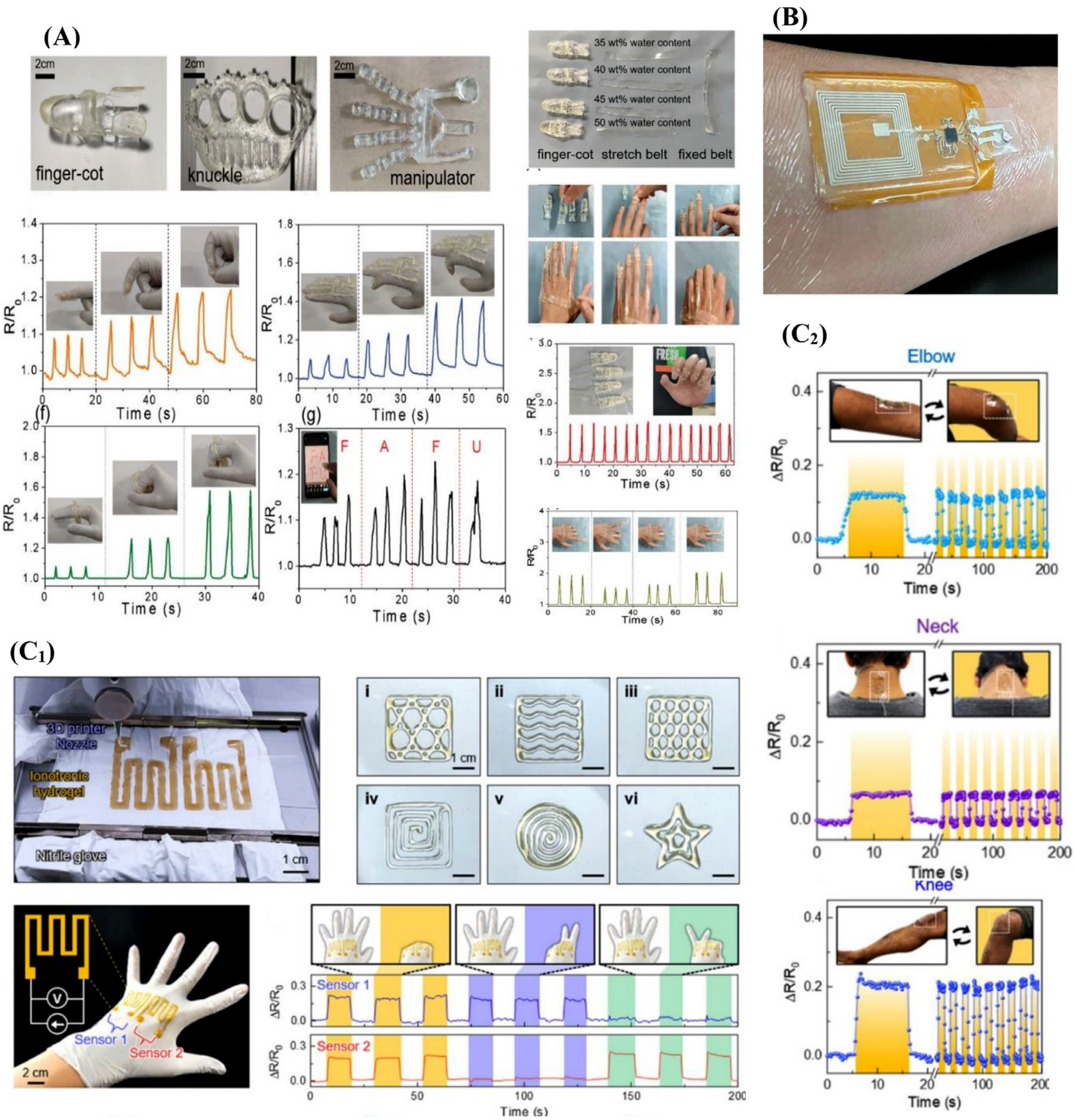


Fig. 16

(A) Various characteristics and functions of 3D-printed hydrogels: customization of wearable sensors and their corresponding resistance responses including finger-cot, knuckle and manipulator. Resistance responses of finger-cot, knuckle, and manipulator, finger-cot sensor depicting handwriting function and its resistance response, printed parts with varying water content, complex manipulator assembling process, flexible sensors measuring resistance responses at finger bending, and hand gestures resistance monitoring by flexible manipulated sensor (adaptedfrom ref. [423] copyright 2021 Wiley-VCH GmbH); (B) the real-time and wireless pH measurement of pH changes through novel sensor system attached to the human forearm (adapted from ref. [424] copyright 2023 Wiley-VCH GmbH); (C_1) Itonotronic PPT hydrogels through 3D printing for wearable strain sensors, DIW of PPT hydrogel, different patterns of 3D-Printed PPT hydrogels, glove-type wearable 3D-printed sensor having two separate strain gage patterns of PPT hydrogels, and strain gage patterns on a 3D-printed glove sensor measuring relative resistance changes under three different bending modes to the fingers, (C_2) Wearable strain sensors for measuring relative resistance changes in repeated bending of various body parts such as the neck, elbow, and knee (adapted from ref. [425] copyright 2023 American Chemical Society).

as suitable ink for 3D printing in food industry applications. Shanthamma et al. [433] used turmeric powder and sago flour material for extrusion-based printing that was later immersed in a sodium bicarbonate (SB) concentration. The effect of pH stimulus due to SB different concentrations on various 3D-printed structures was explored for the time-dependent that shifted color from yellow to orange-red and the conditions were optimized by taking sensory scores. The proposed technique has huge potential to be used in the food product industry.

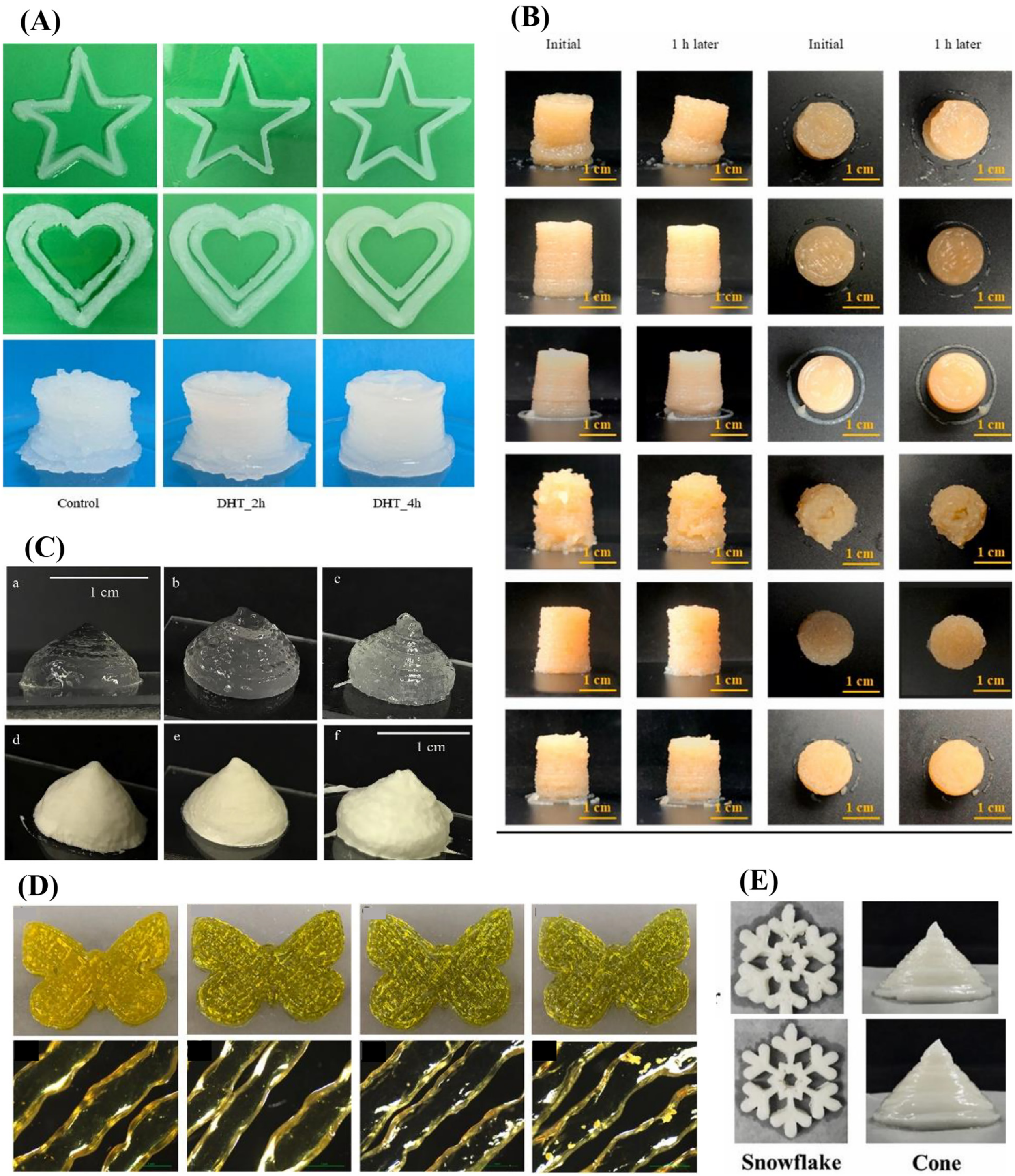


Fig. 17

(A) Various 3D-printed star, heart, and cylindrical shapes hydrogels control wheat starch and improve wheat starch by different dry heating treatments (from left to right) (adapted with permission from ref. [432] copyright 2020 Elsevier Ltd.); (B) Images of various 3D-printed hydrogel samples (front and top views) just after printing and after being placed for 1 h (adapted with permission from ref. [435] copyright 2022 Elsevier Ltd.); (C) 3D-printed geometries (before and after freeze dying) of the various concentration of gelatin-alginate mixture with ratio 2:1. (adapted with permission from ref. [436] copyright 2020 Elsevier Ltd.); (D) Photograph of 3D-printed gelatin hydrogel incorporated with unencapsulated and nanoencapsulated bioactives (adapted with permission from ref. [437] copyright 2021 Elsevier Ltd.); (E) Images of bigels in snowflake (cylindrical and cone models) including front view and vertical view (adapted with permission from ref. [438] copyright 2022 Elsevier Ltd.).

3D printing is now delivering complex architectured foods which are widely attracted by children, and elderly individuals [434]. Moreover, 3D-printed foods also have the ability to preserve key nutrients for healthy intakes, which can easily be swallowed by elderly people and patients. According to Pan et al. [435], soy protein isolate-based hydrogels can be used as a potential 3D-printed food. Insights of this study suggested thermal treatment and Flammulina velutipes polysaccharide addition in hydrogels made them less viscous stable (>99.9%), and stronger, with a more uniform and denser microstructure, as presented in Fig. 17(B). Thus, thermal denaturing soy protein with Flammulina velutipes polysaccharide is effective for the food industry.

Extrusion-based printing was employed by Kuo et al. [436] for fabricating the bioscaffold using gelatin and alginate-based hybrid hydrogels. Texture profile analysis demonstrated excellent hardness and adhesiveness the bioscaffold produced hybrid gels of 7%. The 3D-printed bioscaffold after freeze-drying exhibited reduced water content activity and improved hardness as depicted in Fig. 17(C). Leena et al. [437] explored gelatin-based hydrogel with nanocarriers of zein-based for co-delivery of curcumin and resveratrol for various 3D-printed customized structures, as presented in Fig. 17(D). The added nanoencapsulates of nutraceuticals demonstrated bioaccessibility of 79% for curcumin and 82% for resveratrol in zein-PEG core-shell. Thus, proposed results guided that nutraceutical oral delivery system will be improved with the developed 3D-printed novel nanoparticles-based hydrogel model food with various tailored structures.

Chen et al. [438] prepared bigels systems using a mixture of hydroxypropyl methylcellulose (HPMC) hydrogels and beeswax oleogels. From a 3D printing perspective, prepared bigels with 60% oleogel content flourished printing capability, while inhomogeneity of semi-bicontinuous bigels resulted in poor extrusion capability. The prepared 3D-printed bigels as depicted in Fig. 17(E) can replace conventional solid fat and specific design appearance for food products. It was envisaged bigels systems will be a potent for food 3D printing.

3.5 Electromagnetic interference shielding

Electromagnetic interference (EMI) is used to block interferences and cross-talk for captivating miniaturization of electronics and telecommunications devices [439]. 3D-printed 'intelligent' materials and 'smart' structures have excellent to produce these devices for the aircraft and defense industry [440–442]. Many researchers have attempted to develop EMI using smart structures with polymers and hybrid hydrogels. Menon et al. [443] developed 3D-printed shape memory PU structures with silver coating as depicted in Fig. 18(A) for EMI shielding. Results showed that excellent shape memory properties of PU were further improved due to poly dopamine (PDA) coating and electroless deposition. Thus potential to use as shape memory triggered actuators for EMI applications. However real breakthrough was provided by Liu et al. [444] by developing novel Ti_3C_2-MXene-functionalized conductive hydrogel inks for 3D printing. The proposed MXene/Poly(3,4-ethylenedioxythiophene), polystyrene sulfonate (PEDOT: PSS) hydrogels demonstrated excellent flexibility, stretchability, and mechanical properties such as fatigue resistance. This study provides a unique strategy for fabricating printed hydrogel for customizable EMI-shielding applications, as revealed in Fig. 18(B).

Erfanian et al. [445] proposed that nano-fibrillated cellulose/GO-based hydrogel through DIW has high potential as EMI shielding materials, as presented in Fig. 18(C) and lightweight electronics applications. High-resolution DIW in the proposed study was achieved by treating cellulosic component, with ((2,2,6,6-tetrame-thylpiperidin-1-yl) oxidanyl (TEMPO), resulting in better-quality colloidal dispersion and the rheological properties of inks. Furthermore, higher mechanical properties, such as compression modulus (250–1096 kPa) and EMI shielding (55.6 dB) were reported.

3.6 Anti-counterfeiting

Information safety has always been a threat since ancient times. With globalization, consumers have unprecedented access to products. Consumers, however, have also been exposed to a wide range of counterfeit products as a result of this ease of access [446–448]. Chen et al. [449] reported an interesting approach using 3D-printed (visible light photochemistry) hydrogel objects for direct encryption. The proposed approach is further improved by UV light for activating geometrically complex surfaces, which results in the dissociation of ortho-nitrobenzyl ester units in a spatioselective manner for information coding as presented in Fig. 19(A). This facile and general strategy opens up the possibility of multi-functional 3D-printing of hydrogel origami for data information encryption and protection.

Switchable surfaces are pivotal for many functional materials. It triggers shape morphing behaviors through its dynamic texture but the construction of dynamic surface textures is quite challenging because it involves surface patterning and complicated structural design. The solution to this problem was solved by Li et al. [450] who studied a pruney finger-inspired switchable surface (PFISS) using PDMS having water-sensitive surface textures through DIW. The PDMS had water absorption–desorption characteristics which actuate hygroscopicity of the inorganic salt filler. Results showed that the PFISS demonstrated high water sensitivity similar to human fingertips as presented in Fig. 19(B) with clear surface variation in wet and dry states. Furthermore, the developed PFISS performed a good antislip effect and effective regulation of surface friction. Thus proposed has huge potential to be used in a wide range of switchable surfaces.

Encryption on complex 3D objects holds great promise in information security. For instance, Zhang et al. [451] demonstrated an anti-counterfeiting platform through fluorescent-PVA/gelatin hydrogel. Data encryption capability had extended from single 2D planes to complex 3D hydrogel origami geometries with excellent shape memory, and self-healing properties triggered under borax. Moreover, the 3D anti-counterfeiting platform exhibited superior robustness for data encryption inside complex 3D hydrogel origami structures under UV light immunization, as depicted in Fig. 19(C). Thus, developed multi-functional 3D fluorescent hydrogels can potentially be applied in more reliable encryption products and beyond information protection.

Encryption technologies are critical for anti-counterfeiting as well as information security. It is particularly concerning

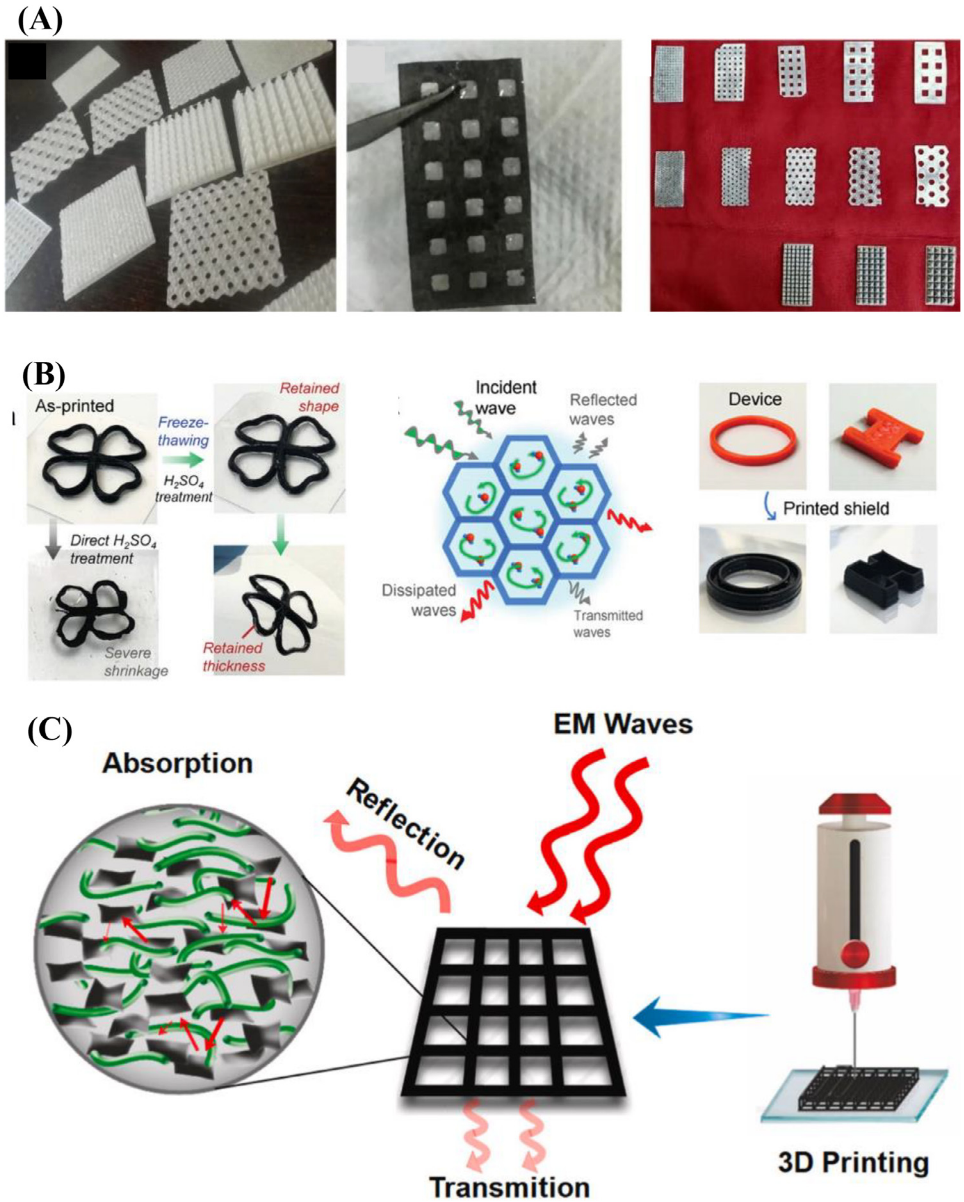


Fig. 18

(A) 3D-printed colorless structures, PDA/PU coated 3 mm square meshes, and 3Dprinted silver and PDA coated structures (adapted from ref. [443] copyright 2023 Royal Society of Chemistry (RSC)); (B) Images of the as-printed architectures before and after various post-treatments, Shielding mechanism schematic illustration, and images revealing the potential of 4D-printed hydrogel structures perfectly fit the target device (adapted from ref. [444] copyright 2021 Wiley-VCH GmbH); (C) Schematic depiction of DIW-based printing of novel cellulose nanofibril/GO ink for EMI shielding (adapted with permission from ref. [445] copyright 2023 Elsevier Ltd.).

when vaccines, antibiotics, and other life-saving commodities are targeted [452,453]. Despite the difficulty of imitating the products themselves, labels and packaging are easily manipulated. There are two common counterfeiting strategies: tampering with the details on authentic packaging (e.g., changing the expiration date), and using authentic packaging to pass off counterfeit products as real [454,455]. Nawaz et al. [456] developed a cellulose acetate-based fluorescent pH sensor for sensing intense acidity and alkalinity conditions using a cross-linking agent such as 4,4′-diphenylmethane diisocyanate (MDI). The prepared material exhibited aqua blue fluorescence and demonstrated extreme pH sensing applications for various pH conditions such as extreme acidic and alkaline pH by visual and fluorescence color change response under a narrow pH range as highlighted in Fig. 19(D). This work holds great promise security printing, and smart food packaging and printing applications.

4 Summary and future outlook

3D printing techniques are now in continuous evolution. With time, new materials and techniques are being discovered, and so as for printers, which will be offering high resolution of printed parts with mass production similar to the casting, rolling and extrusion

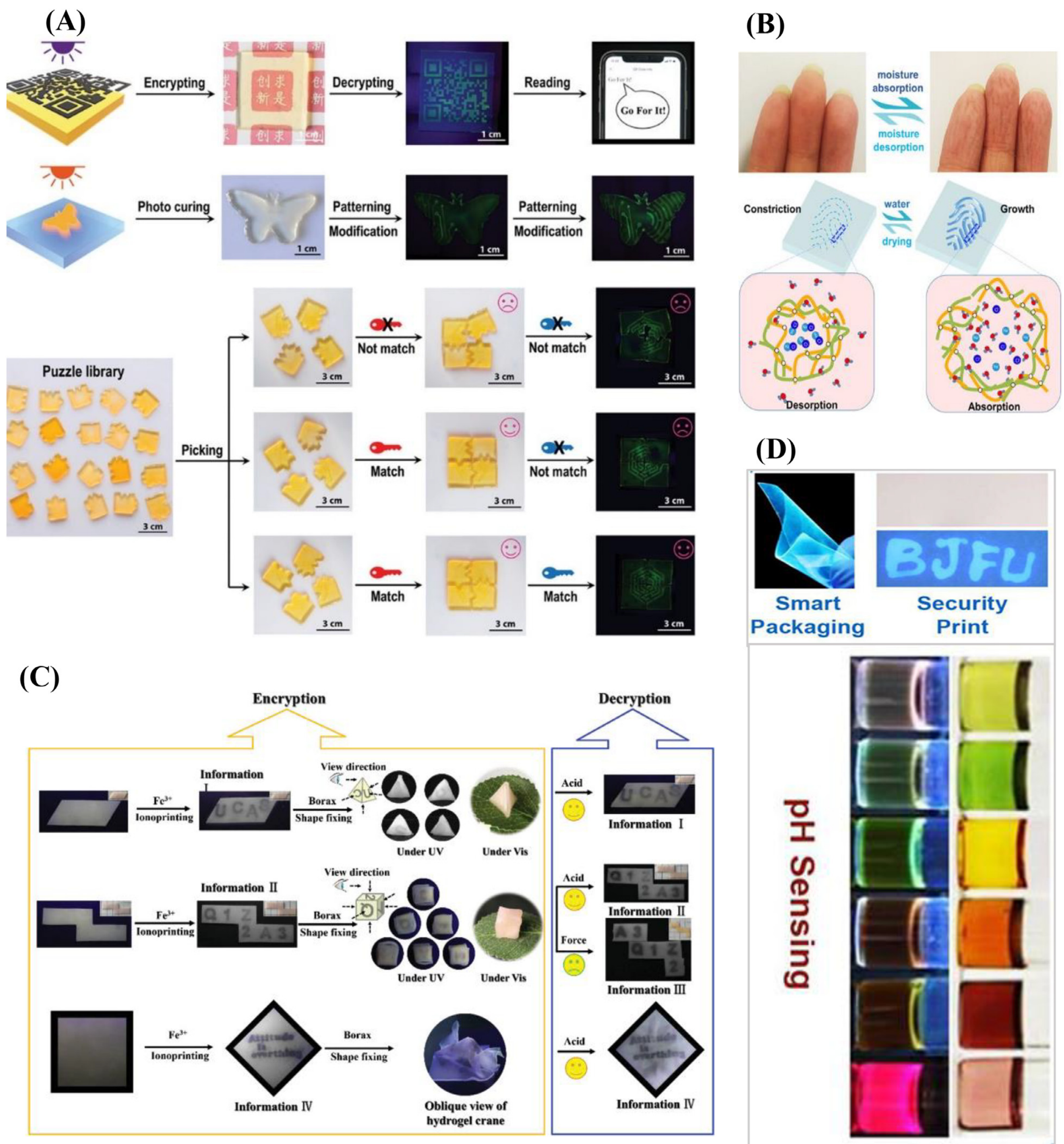


Fig. 19

(A) Encryption and decryption performance of printed hydrogel under a UV backlight source recorded by a conventional camera. Single-stage encryption and decryption processes, butterfly-shaped hydrogel sequence patterning, and multistage encryption using a puzzle library (adapted from ref. [449] copyright 2023 Wiley-VCH GmbH); (B) Design and fabrication of the PFISS-based finger prototype (adapted from ref. [450] copyright 2023 American Chemical Society); (C) Fluorescence-based 3D anti-counterfeiting platform demonstrating through encryption and decryption various messages printed in 2D hydrogel films including "UCAS," "Q1A2Z3," and "Attitude is everything" messages (data were successfully encoded inside the 3D hydrogel geometries) (adapted from ref. [451] copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (D) Developed Lum-MDI-CA solutions for different pH sensing and its potential applications in security printing and smart packaging (adapted from ref. [456] copyright 2023 American Chemical Society).

[457]. Many envision that in the near future, the maturity of bioprinting technologies using hybrid living materials and bio-instructive materials with hydrogels will lead to the production of self-sufficient and self-regenerating structures for biomedical applications [458]. Fig. 20 depicts current challenges and future research directions for 3D-printed SRHs.

Despite the fact that 3D printing uses the least amount of energy from all the traditional manufacturing techniques its

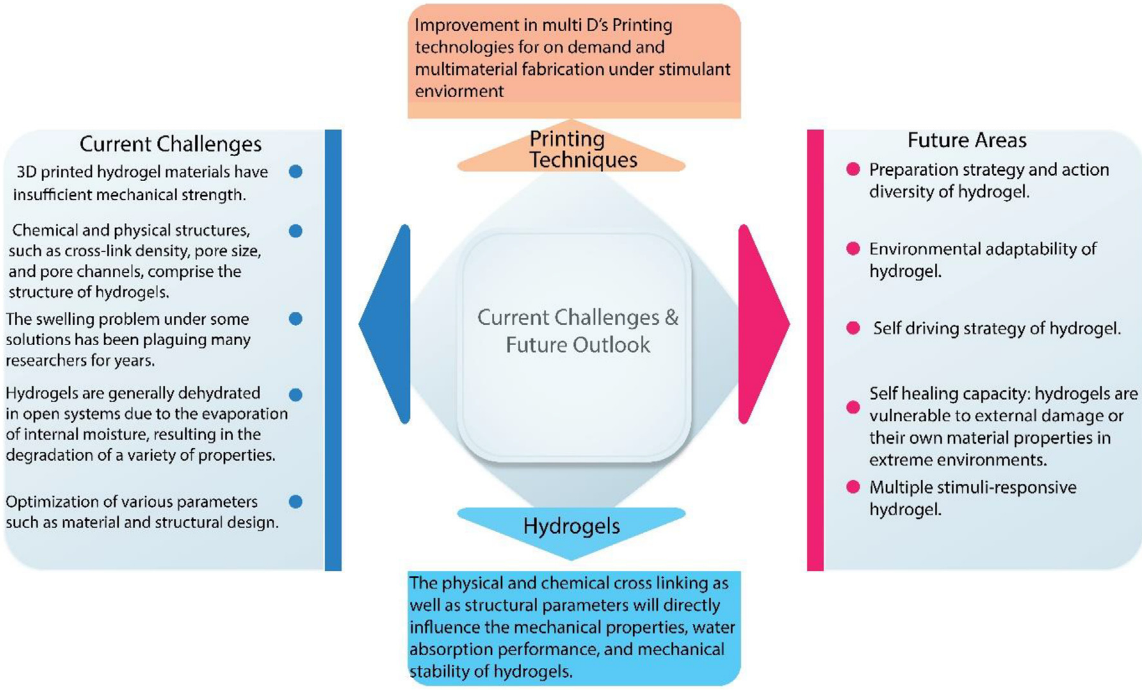


Fig. 20

Current challenges and future research directions in the field of 3D printing of SRHs.

implementation from the design phase to its targeted applications is still complex [459–461]. There is no adaptability or longevity to the current 3D-printed systems. This problem can be solved by naturally-produced hydrogel materials such as starch, chitosan, cellulose, and alginate etc., Naturally, hydrogel materials have the ability to hold a lot of water due to their hydrophilic nature which limits their applications [462–464]. This can be tackled by devising a facile cross-linker and well-controlled polymerization rate for their effective 3D printing, particularly for precisely customized structures in soft robotics applications.

Soft robotics is a fast-growing field [465]. Due to their huge prospects in medical care, complex terrain exploration, and wearable and implantable devices [466]. Moreover, in the last few years, integration and miniaturization have been some of the major challenges faced by researchers today, particularly for soft pneumatic robotics [467–469]. Shape-morphing behavior of stimuli-responsive hydrogel materials has conversely been at the core of large efforts for fabricating novel composite frame–membrane structures to produce untether soft actuators that can sense their motions [470–472]. With the addition of renewable nanomaterials such as cellulose and synthetic graphene, CNTs not only bestow good printability to the hydrogel inks but also solve many issues such as brittleness resulting in more responsive hydrogel structures [473–475]. A broad range of applications could be developed and implemented by combining renewable nanomaterials with hydrogel materials.

3D printing of complex hydrogel structures is quite challenging due to the poor printability of extremely soft materials such as hydrogels in which ideal shear-thinning, and poor shape fidelity of printed patterns are hindering the progress of DIW printing [476–478]. However, these challenges somehow can be resolved by optimizing hydrogels' rheological characteristics. However, the lack of an effective cross-linking strategy which is capable of delivering higher print fidelity with excellent biofunctionality and appropriate yield strength, is still challenging for fabricating cell-laden structures that have great potential to benefit hydrogels bioprinting [479,480]. Various biocompatible and rheological characteristics of hydrogel materials through 3D printing must be explored further to avoid their immature response and any uncontrolled triggering for any unknown stimulant. Thus, researchers need to move with precautions for evaluating all possible mechanisms behind this technology for their complete understanding [481]. Moreover, 3D printing of hydrogels with graphene, CNT, and other nanomaterials for health-related perspective must be considered. For instance, any possible immune response must be evaluated [482]. In addition to that, one further open question in the field i.e., stimuli response of hydrogels can be dangerous and uncontrollable?

Finally, the intended framework capabilities such as controlled platform and high-end simulation have the potential to provide more knowledge on 4D printing and various complex mechanisms, such as metamaterial-based structures in various environmental interactions [483]. Continuous improvement in printing processes through artificial intelligence and machine learning will boost the capability of computational models for both optimizing and improving the performance of printed materials. This area lately has aroused enormous academic curiosity. Thus, the newly evolved frameworks will ultimately design the structural part capable of performing satisfactorily and will meet the practical applications.

We highlighted that applications of 3D-printed hydrogels in anti-counterfeiting, soft robotics, and food industries are still in their infancy and are limited to laboratory scales. We have highlighted some of the main bottlenecks in their vast production particularly through the DIW for printing the actuators with some curvatures and suspended structures, which may collapse in DIW due to the force of gravity. In comparison, TPP, DLP and FDM have various advantages of wide adaptability, no particle sedimentation, low cost, and simple principle. Moreover, in a FDM system, the molten material can be cooled rapidly, which provides support for subsequently printed structures. Thus, the control of the transformations of the complex parts can start mass production on a large scale.

In this review, we introduced a series of SRHs, their shape-morphing mechanisms and their various applications. The classification of SRHs in this review is based on relevant AM techniques where the stimulus mechanism opens up an innovative solution, and discusses the challenges faced by researchers in the respective fields. It is hoped that this review will deepen the understanding of the SRHs including their applications.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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